Thermodynamic state of the laser-induced liquid phase and position of the triple point of carbon

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Quasi-equilibrium and metastable (overheated) liquid phases of carbon are formed in the initial stage of the laser irradiation of a graphite target in air and in a vacuum, respectively, with an approximate position of the solid–liquid–vapour triple point of carbon at 1 bar, 4000 K.

The problem of the thermodynamic state of carbon, in particular, its liquid phase, under high-power pulsed laser irradiation has hardly been studied to date. Meanwhile, for nonequilibrium laser-induced melting and evaporation of a substance, the thermodynamic theory of stability predicts the appearance of a metastable (overheated) liquid phase[1] and, hence, the results of studying physical (optical, thermophysical) properties of a laser-induced graphite melt[2,3] should be, albeit cautiously, related to the parameters of the equilibrium liquid phase.

Under laser irradiation of a graphite target a liquid phase of carbon is formed through a sequence of heating, melting and evaporation processes as well as oxidation. Our estimates of oxidation (burning) front velocity at the surface of the laser-heated graphite target in air were performed using gas dynamics formulae (1) for a collision frequency of gas molecules with the target surface

$$V_{\mathrm{oxid}} = \alpha 2\beta\sigma L N 0.25 V = \alpha\beta\sigma L \frac{P_0}{\sqrt{0.5\pi MkT}} \qquad (1)$$

where α is the sticking coefficient of oxygen molecules on a graphite surface ($\alpha = 1$), β is the oxygen content in air (21%), σ is the cross section of a carbon atom on a graphite surface (1.5×10^{-20} m^2), L is the surface atomic layer thickness (3.35×10^{-10} m), N is the air density at 4000 K (2.5×10^{24} m^{-3}), V is the average velocity of air species at 4000 K (10^3 m s^{-1}), and M is the average mass of air species (5×10^{-26} kg). These estimates exhibited a negligible effect due to the oxidation process (the oxidation velocity value is less than the atomic layer per laser pulse of duration 25 ns). On opposite, heating, melting and evaporation processes are dominant at the laser-induced formation of a liquid phase of carbon occurring *via* different routes in the phase diagram of carbon depending on the value of external pressure P_0 on the target surface (residual gas in vacuum or in air) (Figure 1). Therefore, at the present time, the ambiguity in the determination of the parameters of the solid–liquid–vapour triple point of carbon presented in the literature is the most significant problem for describing the route of formation of the liquid phase of carbon (in the phase diagram of the substance) under conditions of pulse laser irradiation. The points (100 atm, 5000 K)[4–7] and (1 atm, 4000 K)[8,9] in the phase diagram of carbon are presently assigned to the most probable points of the triple point.

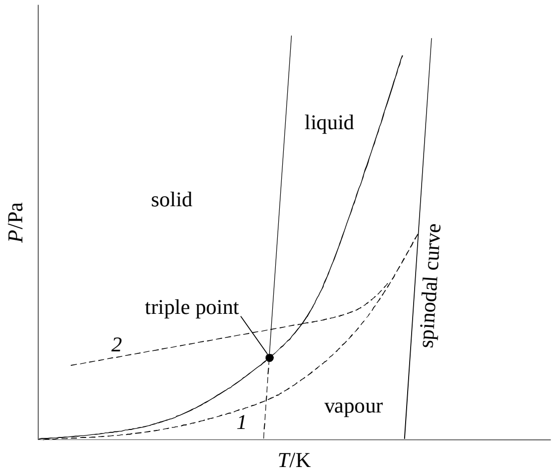

Figure 1 The trajectories of the surface layer state in the schematic phase *P,T*-diagram for the laser heating, melting and evaporation of graphite in a vacuum (*1*) and in air (*2*).

We suppose that the graphite target in a vacuum exists under an external pressure P_0 of residual gas (*i.e.* 10^{-7} torr) and the recoil pressure P_{rec} of laser-evaporated carbon species (in the absence of a ‘graphite–carbon vapour’ equilibrium). The residual gas pressure remains constant with laser heating of the target surface under high vacuum conditions but the recoil pressure, which is equal to approximately one half of the saturated carbon vapour pressure P_{sat} at the given surface temperature T,[10] rapidly increases according to the Clausius–Clapeyron equation with growth of evaporation temperature on the target surface. Hence, the graphite target is hardly evaporated on heating with laser radiation, up to the intersection point of the sublimation curve with the $P(T)$ curve; the $P(T)$ curve describes the total pressure of the residual gas in the Knudsen layer and the recoil pressure P_{rec} of carbon vapour at the temperature of the target surface T (Figure 1, curve *1*).

$$P(T) = P_0 + P_{\mathrm{rec}} = P_0 + 0.5P_{\mathrm{sat}}(T) \qquad (2)$$

On further heating of the graphite target with laser radiation, starting from the sublimation curve, one cannot neglect the evaporation of the target, which produces a considerable recoil pressure of carbon vapour on the target surface. The temperature dependence $P(T)$ of the overall pressure of the residual pressure and recoil pressure of carbon vapour is presented in the phase diagram below the sublimation curve. It therefore corresponds to the absence of mechanical equilibrium on the target surface and the co-existence of a metastable (overheated) solid in the gas phase with a nonequilibrium composition (Figure 1, curve *1*).

When the representative point for the thermodynamic state of the graphite target surface layer moves along the $P(T)$ curve, it asymptotically reaches the curve $0.5P_{\mathrm{sat}}(T)$. The last curve at certain pressure and temperature values crosses the curve of co-existence of the metastable (overheated) phases of solid and liquid for carbon, which continues the corresponding curve of co-existence of the equilibrium phases of the solid and liquid to a region lower than the triple point. Thus the metastable (overheated) phase of liquid carbon is formed on the target surface and its evaporation under laser irradiation follows along the $0.5P_{\mathrm{sat}}(T)$ curve to the spinodal curve of the carbon liquid phase (Figure 1).

Different routes of formation of the carbon liquid phase in the case of evaporation in air (P_0 = 1 bar) may occur depending on the position of the solid–liquid–vapour triple point for carbon (1 or 100 bar) since the residual gas (air) pressure in the Knudsen layer can exceed the corresponding pressure P_{tr} of carbon vapour in the triple point. We assume the pressure of the heated air in the near-surface layer of 10^{-6} m thickness remains constant (1 bar) with the surface temperature growth due to fast (10^{-9} s) acoustic off-loading of the layer and the increase of the $P(T)$ is mainly concerned with the recoil pressure growth [the

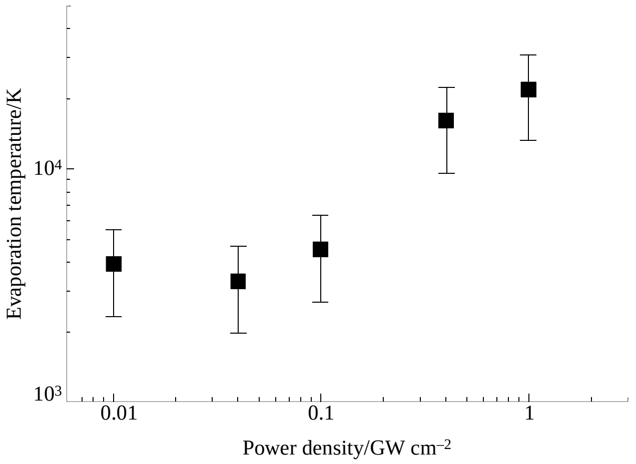

Figure 2 Evaporation temperature of the polycrystalline graphite *versus* laser power density.

$0.5P_{sat}(T)$ term in the expression (2)]. In this case, laser heating and evaporation of the graphite target results in the formation of a quasi-equilibrium phase of the carbon melt on the target surface under an external pressure $P(T) > 1$ bar. The intersection of the $P(T)$ curve with the curve of liquid–vapour equilibrium takes place near the triple point of carbon [at $P(T) = 2$ bar according to equation (2)]. Further laser evaporation processes follow the $P(T)$ curve in the region of the metastable (overheated) liquid phase of carbon [$P(T) \approx 0.5P_{sat}(T) < P_{sat}(T)$] up to the spinodal curve for the liquid phase (Figure 1, curve *2*).

At the present time, it is established that laser-irradiated graphite begins to melt in air at the threshold power density $I_0 = 0.02$ GW cm^{-2} of laser radiation with a nanosecond duration.[3,11] The chaotic arrangement of crystallites in the melting/recrystallisation region of highly-oriented pyrolytic graphite was identified by transmission electron microscopy.[11] Interference of the heating (probing) laser radiation observed for angular dependence of the reflection coefficient of the polycrystalline graphite target at power density values above the melting threshold value has also confirmed production of the surface graphite melt layer under the laser irradiation.[3] The published data on the parameters of the thermodynamic state of the graphite surface (4000 K, 10 bar)[12] within the laser pulse at $I_0 = 0.02$ GW cm^{-2} are in reasonable agreement with our estimates of the total gas pressure $P(T)$ at this temperature of the target surface (1–2 bar) obtained according to equation (2). The facts presented indicate that laser heating of the graphite target passes through a quasi-equilibrium melting stage of the material at the parameters of the triple point of carbon $T_{tr} \approx 4000$ K, $P_{tr} < 10$ bar.

In the present study of the composition of positively charged products of laser thermal evaporation of polycrystalline graphite using a laser setup [laser radiation wavelength 532 nm, pulse energy 5 mJ, pulse duration (FWHM) 25 ns, repetition rate 12.5 Hz] and a time-of-flight mass spectrometer described previously,[13] we determined the evaporation temperature of carbon in a vacuum as 4000±1200 K (Figure 2) from the half-width of the Maxwell distribution of primary ion velocities. The thermal emission mechanism of the primary ion yield and the effusive movement of the charged species under a carbon plume pressure lower than 1 bar were assumed for the temperature calculations. The range of I_0 (0.01–0.1 GW cm^{-2}) in which the evaporation temperature values were calculated undoubtedly covers the threshold value of the laser power density for the transition of the overheated solid to the overheated liquid in a vacuum, because the last one is close to the I_0 value for graphite melting in air (0.02 GW cm^{-2}). Since the curve of co-existence of the overheated solid with the overheated liquid moves (in the phase diagram of carbon) from the triple point almost vertically down, the established value of the evaporation temperature of the overheated substance at 4000±1200 K can be considered as a reasonable estimate for the temperature of the triple point of carbon.

Thus, the analysis of the experimental data on the thermodynamic parameters of the laser melting of graphite suggests that the parameters of the triple point of carbon (4000 K, 1 atm) given[9] as the result of statistical processing of the whole mass of available published data agree satisfactorily with the data presented in this work. Regarding the method of formation of the liquid carbon phase under the the pulsed laser irradiation of graphite, this position of the triple point of carbon implies that on laser heating of graphite in air the liquid phase is formed under quasi-equilibrium conditions, and when graphite is evaporated in a vacuum, it is formed from the metastable (overheated) solid phase of carbon.

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Received: Moscow, 3rd April 1998
Cambridge, 10th June 1998; Com. 8/02793E