Optical feedback in laser-induced phase transitions of carbon

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Owing to interference of laser radiation in a film of liquid carbon on the surface of graphite, the change in the film thickness apparently controls the dynamics of laser-induced phase transitions (melting and evaporation) of carbon.

In the light of the latest data about the dielectric character of the optical properties of liquid metals,[1,2] the theory of laser-induced phase transitions (LIPT) in metals and metal-like materials seems far from being well developed.

Up to date, a number of important functions of the liquid phase in LIPT have been established. The necessity to take into account the surface melt made it possible to disprove the view[3] that the surface of a target can be heated monotonically above critical temperature T_{cr} up to $T \sim \Delta_{evap}H \sim 10T_{cr}$; it was found that temperatures $T > T_{cr}$ can be achieved only in vapours as a result of efficient absorbance of radiation.[1] The film of the melt also plays a crucial role in the feedback mechanism of the velocity of propagation of phase transition fronts, the particular mechanism of the influence of properties of the melt being determined by the α/χ ratio assumed in the model.

If the melt is characterised by a 'metallic' type of properties (large α/χ values), a liquid phase with thickness χ/V_{evap}^2 of up to 10^{-3} cm is formed as a result of propagation of the heat wave deep into the target,[1] and thermal resistance of the liquid layer acts as the key factor in the feedback mechanism.[4] This parameter determines the heat flux directed at the melting front in the bulk of the target and thus controls the temperature of the surface and the rate of evaporation. When this feedback mechanism operates during a free-generation laser pulse, the LIPT dynamics reach a steady-state regime with constant velocities V_{evap} and V_{melt} and a constant thickness of the melt Y_{st}.[4]

The role of optical feedback in dielectric oxide melts during laser-induced oxidation of metals has been noted previously.[5] It was found that due to interference of the radiation in the metal oxide film, its reflectance and transmittance vary as a function of the film thickness, and instantaneous values of these parameters control the chemical transformation.

For LIPT in metals, the optical feedback has been considered in the context of 'metal–dielectric' phase transitions.[1] In the case where formation of the dielectric phase during metal–dielectric transition is characterised by a threshold T_{md} (I_{md}), the reflectance coefficient of the medium sharply diminishes at $I = I_{md}$; this causes an acceleration of the evaporation front propagation followed by a flattening out of the dependence of V_{evap}, since the temperature of the surface of a transparent dielectric cannot markedly exceed the temperature of the metal–dielectric transition, $T_{md} \leq T_{cr}$. The predominant part of the energy flux is at the 'transparency' wave front deposited in the melt.

In the present study, we consider the mechanism of optical feedback in the LIPT dynamics in relation to graphite characterised by 'metal-like' thermal and optical properties. This specific feature of graphite made it possible to apply some elements of the theory of the 'thermal' mechanism of destruction of materials to the description of the LIPT dynamics in the 0.01–0.3 GW cm^{-2} range of radiation intensity.[3]

A significant point in the description of the LIPT dynamics is that carbon melt is a dielectric material over the optical region [n(532 nm) = 1, k(532 nm) < 0.5,[6] n(532 nm) = 0.84±0.01, k(532 nm) = 0.45±0.15[2]], *i.e.* it is characterised by a small α/χ value. Therefore, the role of heat conduction of the liquid film is insignificant compared to that of the change in the optical properties of the air–melt–graphite layered medium, which depends on the velocities of propagation of the melting and evaporation fronts *via* individual optical characteristics of liquid carbon and the instantaneous thickness of the melt film.

When a carbon surface is heated by laser radiation up to the temperature of the graphite–liquid–vapour triple point T_{tr} (*ca.* 5000 K), phase transition fronts, melting and evaporation, start to propagate deep into the material. In the case of a moderately absorbing graphite melt [α(532 nm) = (8±3)×10^4 cm^{-1}] with a low heat conductivity, the movement of the melting front deep into the target is maintained as a result of heating and melting of graphite at the phase interface, owing to absorbance of the radiation that has passed through the melt by the solid phase, whereas the movement of the evaporation front is maintained owing to the absorbance of radiation in the melt phase. Since the velocities of propagation of the fronts depend on the heats of the transition [ΔH(liq., P_{tr}, T_{tr}) = 200 kJ mol^{-1} and $\Delta_{evap}H(P, T)$ = 265 kJ mol^{-1}],[7,8] the melting front overtakes the evaporation front, and the film of liquid carbon appears. In turn, owing to interference of the radiation, the thickness of the melt film Y determines the reflectance (R), transmittance (T) and absorbance (A) of the air–melt–graphite layered medium and has an influence on the velocities of propagation of the phase transition fronts.

In this study, we describe the variation of the film thickness during the laser pulse with a power density much higher than the threshold value needed for graphite to melt (0.02 GW cm^{-2}) by equation (1).

$$\frac{dY}{dt} = V_{melt}(t) - V_{evap}(t) \quad (1)$$

According to the overall balance of the fluxes on the surface of the material, the light flux coming from the gas phase is partially reflected by the melt film; it warms up and evaporates the liquid film with a heat of $\Delta H_{eff}(P, T)$ [$\Delta_{evap}H(P, T) + \Delta H$(liq.; P_{tr}, $T_{tr} \rightarrow P, T$)], whereas that part of the flux that passes through the film is spent in maintaining the movement of the melting front and heat wave in the solid. Thus, the boundary condition for the Stefan problem for the melting front velocity has the following form (V_m is the molar volume of graphite)

$$V_{melt}(t) = \frac{T(Y)I(t)V_m}{\Delta H(\text{liq.}; P_{tr}, T_{tr})} \quad (2)$$

and the velocity of the evaporation front can be expressed as follows

$$V_{evap}(t) = \frac{[1 - R(Y) - T(Y)]I(t)V_m}{\Delta H_{eff}(P, T)} \quad (3)$$

Taking into account equations (2) and (3), equation (1) can be written as equation (4):

$$\frac{dY}{dt} = \frac{T(Y)I(t)}{\Delta H(\text{liq.}; P_{tr}, T_{tr})} - \frac{[1 - R(Y) - T(Y)]I(t)}{\Delta H_{eff}(P, T)} \quad (4)$$

We can find a particular solution for this equation for the initial condition $Y(0) = 0$ if we express the $R(Y)$ and $T(Y)$ dependences for a moderately absorbing film in terms of the theory of multiple reflections in layered media,[9] *i.e.* by the

function $X(Y) = X_0\exp(-2\alpha Y)$ (where α is the absorbance coefficient and the term X_0 is determined by the refraction n and attenuation k indices of the contacting phases).

The main physical processes and regimes of destruction of a carbon target through evaporation at high temperatures can be found from an analysis of equation (4) if it is written in the following form

$$F(Y) = \frac{T(Y)}{\Delta H(\text{liq.}, P_{tr}, T_{tr})} - \frac{[1 - R(Y) - T(Y)]}{\Delta H_{eff}(P, T)} \quad (5)$$

The steady-state regime for the evaporation destruction of the melt film is described by the expression $V_{melt}(t) = V_{evap}(t)$ [$F(T) = 0$]. The influence of the melting and evaporation processes result in a steady-state film thickness over a radiation pulse of the Gaussian shape with duration $\sqrt{2\pi}\tau$ being established, equation (6), where $B = 2\sqrt{2}\alpha\tau I_0 V_m \Delta H_{eff}(P, T)^{-1}$

$$Y(t) = \frac{\ln[(T_0(1 + \frac{\Delta H_{eff}(P, T)}{\Delta H(\text{liq.}, P_{tr}, T_{tr})}) + R_0)(1 - \exp\{-B\text{erfc}(t/\sqrt{2}\tau)\})]}{2\alpha} =$$

$$= Y_{st} + (2\alpha)^{-1}\ln(1 - \exp\{-B\text{erfc}(t/\sqrt{2}\tau)\}) \quad (6)$$

The rate at which the steady-state regime is established is determined by the parameter B; the main terms in this parameter are α, I_0 and $\Delta H_{eff}(P, T)$. For the steady-state regime to exist, optical (n, k) and thermodynamic [$\Delta H_{eff}(P, T)$] properties of the melt should be invariable.

When the sign of $F(Y)$ is positive [$V_{melt}(t) > V_{evap}(t)$], this corresponds to a non-steady-state growth of the film during the radiation pulse at high transmittance for a moderately absorbing melt film or at large $\Delta H_{eff}(P, T)$. This effect can be realised in the case of a 'metal–dielectric' phase transition at high melt temperatures when a 'transparency' wave propagates in the melt of a metal.[1] If we take into account the weak absorbance in this non-ideal dielectric, we obtain, with slow evaporation, a limited growth of the film thickness owing to the radiation absorbance in the film

$$Y(t) = (2\alpha)^{-1}\ln[2\sqrt{2}\alpha\tau T_0 I_0 V \Delta H(\text{liq.}, P_{tr}, T_{tr})^{-1}\text{erfc}(t/\sqrt{2}\tau)] \quad (7)$$

In turn, the negative sign of $F(Y)$ means destruction of the melt film during the radiation pulse owing to the high velocity of movement of the destruction front; the latter can be accounted for by the low heat of the process or by the low transmittance and reflectance of the film. One of the most probable reasons for the appearance of this regime is the sharp decrease in $\Delta H_{eff}(P, T)$ near the spinodal curve to $\Delta H(\text{liq.}; P_{tr}, T_{tr} \rightarrow P, T)$.[10]

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