Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1996, **6(5)**, 180–181
Mendeleev Communications

Thermodynamics of laser evaporation of polycrystalline graphite

Sergei I. Kudryashov,* Nikita B. Zorov, Aleksandr A. Karabutov and Yurii Ya. Kuzyakov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 939 0701

The change in recoil pressure of polycrystalline graphite as the radiation intensity increases during laser pulse evaporation is related to the movement of the surface as a dynamic system along the curve of the liquid–vapour equilibrium above the triple point of the phase diagram of carbon.

Carbon nanostructures have recently become one of the most interesting objects for various fields of natural science due to their unusual topological, electric and chemical properties.[1,2] Nanospheres and nanotubes are the metastable state of carbon in the form of clusters, occupying an intermediate position between small molecules and macroscopic material. New forms of material, which have no analogs in nature and which possess unique properties, can be obtained at the level of clusters.[3]

Presently, the optothermodynamic method[4] is the only means of studying the thermodynamics of metastable states of carbon in the range of high temperatures and pressures. This ability is related to the unique ability of powerful pulse lasers to heat a substance to hundreds of thousands degrees and to develop a recoil pressure of several hundred megabar.[5]

It is known that the equilibrium solid state of carbon under normal conditions is graphite, which evaporates by a thermal mechanism owing to the metallic character of its thermal and electric conductivity as determined by the absence of a forbidden band between the valence and conductivity band of the valence p-electrons in its band spectrum.[6] The laser surface evaporation of graphite is quasi-stationary if the intensity of incident light I_L is lower than the threshold of explosive boiling of carbon (10^{10} W cm^{-2})[7]; this is based on the assumption that the local thermodynamic equilibrium is controlled by the usual thermodynamic variables and described by the thermodynamics of non-equilibrium processes. This allows one, starting from the known thermophysical and optical parameters of the material, to establish the correspondence between thermodynamic variables (pressure of saturated vapour p and temperature T) of the phase diagram and the analogous parameters of the material upon its evaporation.[8] Thus, the instant recoil pressure P_{rec} corresponds to the pressure of unsaturated vapour at the given instant temperature of the surface and can be expressed[7] as:

$$P_{rec} = \rho_{vap} V_{vap}\ V_{vap} = \rho V_{evap}\ V_{vap}$$

taking into account the continuity equation on the surface:

$$\rho V_{evap} = \rho_{vap}\ V_{vap}$$

where V_{vap} is the velocity of sound in the vapour, V_{evap} is the velocity of the evaporation front in the substance, ρ is the condensed phase density and ρ_{vap} is the vapour density.

The main equation of the quasi-stationary approximation, relating the saturated vapour pressure and the temperature in the surface layer to the parameters of laser radiation and individual characteristics of the medium, is

$$(1-R)I_L V_{vap}/H_{gas}(p,T) = P(T) = P_0 \exp[-\lambda\ (RT)]$$

which is obtained from the boundary condition of the Stephan's problem,[7] taking into account the expression for the recoil pressure and neglecting the heat flow to the bulk medium compared to the heat flow to the surface (which maintains evaporation). Here P_0 is the parameter characterizing the change in pressure as the temperature increases, λ is the heat of evaporation, R is the reflection coefficient and H_{gas} is the heat of transition from the solid-phase state under normal conditions to the gaseous state at the given p and T.

In this work polycrystalline graphite (PCG) with a density of $\rho = 1.7$ g cm^{-3}, consisting of weakly bound graphite grains 0.1 to 100 μm in size, each of which is a batch of individual crystallites ranging 50 to 500 A, was used as a carbon target for evaporation.[9]

The dynamics of evaporation of PCG is determined by the reflection coefficient of radiation R and the heat of transition of the material from the solid-phase to the gaseous state, H_{gas}. The reflection coefficient of PCG under normal conditions is 0.6,[10] but decreases to 10–20% of the initial value on heating the surface to its melting point[7] and becomes equal to 0.1.

The heat of transition of the medium from the solid-phase state under normal conditions to the gaseous state at the given p and T in the range of the liquid–vapour phase equilibrium between the triple ($T_{tr} = 4100$ K, $P_{tr} = 100$ atm) and critical points ($T_{cr} = 6800$ K, $P_{cr} = 2220$ atm) changes from 5.1×10^5 to 7.8×10^5 J mol^{-1}, and the average heat of evaporation of graphite, $\lambda(p,T) = 2.5\times10^5$ J mol^{-1}, is equal to the jump in enthalpy of the medium under transition defined by the equilibrium curve.[8]

The opticoacoustic setup described in refs. 11 and 12 was used in the experiments. The graphite target was evaporated by irradiation with a Nd:YAG laser ($\lambda = 532$ nm) with a pulse duration (FWHM) of 10 ns and a pulse frequency of 0.9 Hz. An integral amplitude of the longitudinal acoustic compression wave (ablative component) for a half-time of the compression pulse for various values of radiation intensity in the I_L range of $(0.1–2.5)\times10^8$ W cm^{-2} was measured by a

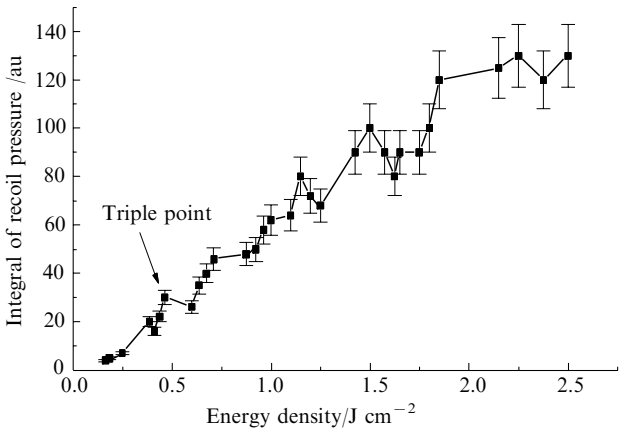

Figure 1 Dependence of the integral recoil pressure on the density of radiation energy.

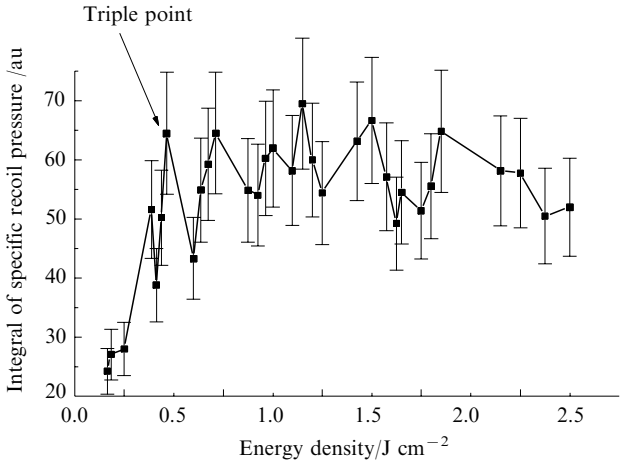

Figure 2 Dependence of the specific value of integral recoil pressure on the density of radiation energy.

piezoelectric ceramic detector in the regime of idle running. An electric signal proportional to the shift of the detector surface for the half-time of the compression wave was recorded by a broad-band storage oscilloscope with a storage of 50 pulses. According to the procedure described in ref. 11, for the intensity values of 1.65 and 2.1×10^8 W cm^{-2}, the average depth of the crater per pulse was measured for a thousand pulses and was 0.13±0.02 and 0.20±0.02 μm. The obtained dependence of the integral recoil pressure on the energy density, as well as that referred to the energy density, are presented in Figures 1 and 2.

The dynamics of the change in phase of the surface layer of the medium several interatomic distances in width is determined by the instant temperature field in the layer and the field of mechanical stresses of the recoil pulse according to the Clausius–Clapeyron equation. The surface medium as an open system moves along the solid/liquid–vapour equilibrium curve. According to the main equation, the system reaches the triple point (T_{tr} = 4100 K, P_{tr} = 100 atm, velocity of sound in the vapour is 1.2×10^3 m s^{-1}) at the intensity of incident light of 5×10^7 W cm^{-2}, which agrees well with the literature data.[12–14] At these values of radiation intensity, the curves in Figures 1 and 2 undergo the breaks typical of the transition from sublimation to evaporation[8] and have the forms typical of the laser evaporation of metals.[7] The enthalpy of transition calculated from the average depth of the crater per pulse for the intensities of 1.65 and 2.1×10^8 W cm^{-2} was 615±100 and 600±100 kJ mol^{-1}, which corresponds to a recoil pressure of 300 bar and a surface temperature of about 5000 K. Above the triple point, the system moves along the liquid–vapour equilibrium curve to the critical point (T_{cr} = 6800 K, P_{cr} = 2220 atm), which is reached for the enthalpy of transition of 7.8×10^5 J mol^{-1} and the velocity of sound in the vapour of 1.7×10^3 m s^{-1} at a radiation intensity of (9–10)$\times10^8$ W cm^{-2}.

At the same time, the nonmonotonous character of the change in the integral value of recoil pressure with increasing intensity does not fit within the range of the experimental error. This effect can be related to the heat instability of the evaporation front[15] for relief heterogeneities 10 to 500 A in size (for comparison, the size of individual crystallites is less than 500 A).[9] At the given radiation intensity, the maximum contribution to the perturbation of the evaporation front is made by the particular component of the Fourier spectrum of the relief irregularity, whose wavelength decreases as the intensity increases and at the critical point becomes equal to the interatomic distance in liquid carbon. The heat instability of the interface is typical of dispergation and results in a lower effective heat of evaporation.[15]

This work was in part supported by the Russian Foundation for Basic Research (grant no. 96-03-33324A).

References

1 P. W. Fowler, *J. Phys. Chem. Sol.*, 1993, **54**, 1824.
2 B. I. Dunlap, *Phys. Rev., B*, 1992, **46**, 1933.
3 H. W. Kroto, A. W. Allaf and S. P. Balm, *Chem. Rev.*, 1991, **91**, 1213.
4 F. V. Bunkin and M. I. Tribel'skii, *Usp. Fiz. Nauk*, 1980, **130**, 193 (*Phys. Usp.*, 1980, **23**, 105).
5 N. B. Delone, *Vzaimodeistvie lazernogo izlucheniya s veshchestvom* (*Interaction of laser radiation with materials*), Nauka, Moscow, 1989, p. 258 (in Russian).
6 F. Bassani, *Elektronnye sostoyaniya i opticheskie svoistva v tverdom tele* (*Electronic states and optical properties in solid state*), Nauka, Moscow, 1982, p. 45 (in Russian).
7 S. I. Anisimov, Ya. A. Imas, G. S. Romanov and Yu. V. Khodzhko, *Deistvie moshchnogo lazernogo izlucheniya na metally* (*Action of powerful laser radiation on metals*), Nauka, Moscow, 1970, ch. 3 (in Russian).
8 M. A. Sheindlin, *Teplofizika vysokikh temperatur*, 1981, **19**, 630 (in Russian).
9 A. R. Ubellode and F. A. Lewis, *Grafit i ego kristallicheskie soedineniya* (*Graphite and its crystalline compounds*), Mir, Moscow, 1965, p. 55 (in Russian).
10 F. Bassani, *Phys. Rev.*, 1969, **178**, 1340.
11 R. O. Esenaliev, A. A. Karabutov, N. B. Podymova and V. S. Letokhov, *Appl. Phys., B*, 1994, **59**, 73.
12 S. I. Kudryashov, N. B. Zorov, A. A. Karabutov, S. V. Kuznetsov and Yu. Ya. Kuzyakov, *Izv. Russ. Akad. Nauk, Ser. Fiz.*, 1996, **3**, 5 (in Russian).
13 J. J. Gaumet, A. Wakisaka, Y. Shimizu and Y. Tamori, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1667.
14 R. W. Dreyfus, R. Kelly and R. E. Walkup, *Nucl. Instr. Meth. Phys. Res., B*, 1987, **23**, 557.
15 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).

Received: Moscow, 20th February 1996
Cambridge, 2nd April 1996; Com. 6/01374K