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Electric probe detection of large cluster ions in spinodal decomposition of the laser-induced labile liquid phase of carbon

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The electric probe procedure developed here has made it possible to detect for the first time large cluster ions, the products of spinodal decomposition of the laser-induced labile state of the liquid phase of carbon, with a size up to a million atoms and relative content in the mass distribution of the order of ppm.

In recent decades, interest in the problem of preparing nanocrystalline materials has significantly increased, because it has been found that a decrease in the crystallite size lower than some threshold value (of the order of magnitude of 10 nm) results in a considerable change in the optical, magnetic and elastic properties of the material.[1] At the present time, compacting of isolated nanoclusters, crystallisation of amorphous alloys and intense plastic deformation of materials[2–4] are the main methods for the preparation of nanocrystalline materials.

Spinodal decomposition of the thermodynamically unstable (labile) state of the liquid phase of a substance is one of the methods used for preparing isolated nanoclusters formed as nuclei of the liquid phase.[5] Macroscopic effects related to the spinodal decomposition of the laser-induced labile state of the liquid phase of carbon were considered previously;[6] however, the composition of spinodal decomposition products has not been studied to date.

So far, the study of the high mass distribution of cluster ions is restricted by the limited range of detected masses for most of the commercially available time-of-flight mass spectrometers. Upper values of detected masses M for the instruments are not usually higher than 10^4 a.m.u. due to the low sensitivity of the detection systems used (secondary electron multipliers, multichannel plates)[7] in the high mass range due to the low efficiency of ion-electron conversion $\eta \sim M^{-0.5}$.[8] Electric probe detection has not previously been used for detecting large cluster ions because of low mass resolution; nevertheless, it has considerable advantages for studying the general modal character of the mass distribution: the η value is close to unity regardless of the mass of the detected ion and the position of the electric probe (collector) near the target ablated by laser radiation allows the sensitivity of the detection system to be further increased due to the corresponding increase in ion collection efficiency.[9]

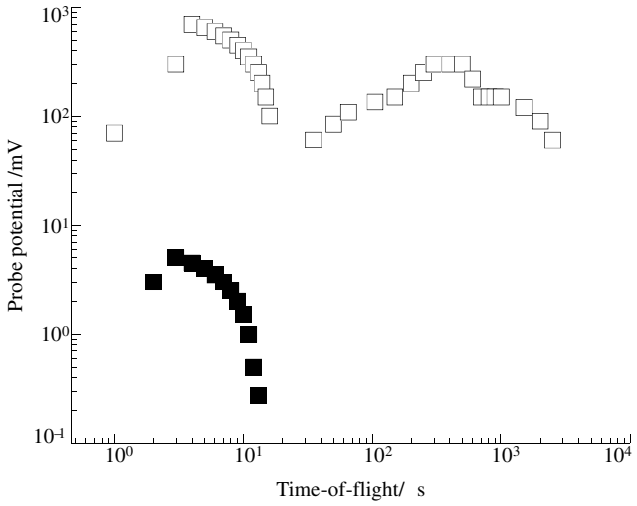

Figure 1 Time dependence of the induced pulsed negative image potential on the probe (extracting/accelerating grid) in the laser evaporation of polycrystalline graphite: laser power density (GW cm^{-2}) 0.19 (dark squares) and 0.36 (light squares).

These advantages of the electric probe method were used in this work to study the high mass cluster ion distribution of the gas phase spinodal decomposition products in the laser evaporation of graphite. A graphite target was evaporated using the radiation from the second harmonic of a Nd:YAG laser (532 nm, 25 ns, 12.5 Hz) with an energy of 5 mJ. After attenuating by neutral filters, the laser radiation was focused by a lens (F = 28 cm) through a quartz window to a vacuum chamber (the residual gas pressure was 10^{-7} Torr) onto the ground rotating ring-like graphite target, perpendicularly to the surface. Part of the laser radiation was directed to a photodiode and pyroelectric plate by a beam splitter in order to synchronise the system of detection and to control the energy of the laser radiation per pulse. The ion optics of a commercial quadruple mass spectrometer (MX-7304) were modified for recording the time-of-flight mass spectra and electric probe measurements.[10] The extracting/accelerating grid of the instrument was used as a collector in the probe measurements and was placed at a distance of 4 cm from the target at a slight angle (10–15°) to the incident laser beam. For detecting negatively charged ions, a constant positive potential of +33 V was applied to the grid relative to the ground graphite target. During detection of the signal the negative pulsed component of the probe potential $U(t)$ was determined by the image potential induced by the negatively charged component q_0 of the evaporated substance in the detecting circuit (time constant of 0.11±0.02 s). Time dependences of the probe potential (Figure 1) were observed and detected at various laser power density values using a S8-12 storage oscilloscope.

The quantitative interpretation of pulsed image potentials measured by the electric probe technique is usually a very difficult

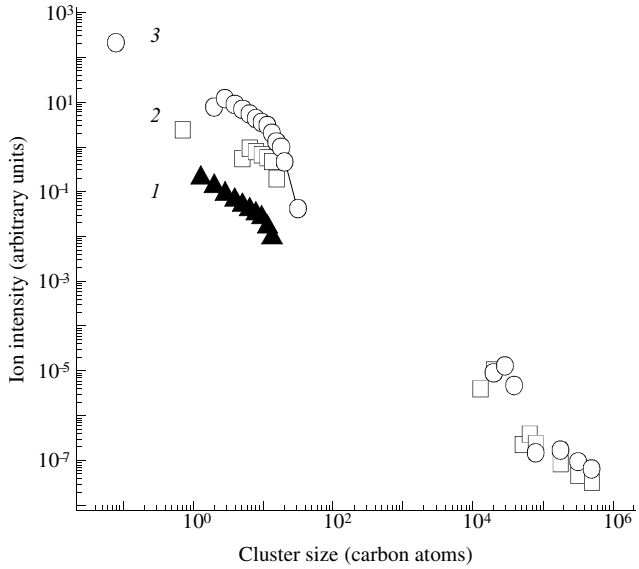

Figure 2 Size (N'/z) distribution of negatively charged cluster ions from measurements of the probe potential [power density (GW cm^{-2})]: (*1*) 0.21, (*2*) 0.33 and (*3*) 1.2.

problem.[9] In this work the approximation of a steady-state (slow) discharge of primary ions of a laser plume (the average power P released in the detecting circuit is close to zero) was developed and used for processing the time dependences obtained for the pulsed probe potential in its delay regions (Figure 1). Our assumption about the steady-state plume discharge was based on the following facts: i, the delay of the signal (discharge phase) lasts long enough (more than 7 ms) as compared with the arrival time of the low mass ions (~1–10 s); ii, this region of the signal is smooth thus corresponding to a nearly monotonous change in the size distribution of the cluster ions. The condition of steady-state discharge of cluster ions ($P \approx 0$) for the expression of the power

$$\frac{dW}{dt} = P = \frac{d(qU)}{dt} = U\frac{dq}{dt} + q\frac{dU}{dt} \quad (1)$$

(where W is the energy released in the detecting circuit, and q and U are the charge and potential, respectively, induced in the detecting circuit) can be written as the condition of energy balance on the surface of the detecting electrode

$$U_0\frac{dq}{dt} = -q_0\frac{dU}{dt} \quad (2)$$

where U_0 and dU are the electrode potential and its change during the discharge of cluster ions with dq charge and q_0 is the overall charge of all detected ions.

Using equations (1) and (2), we can describe the dynamics of discharge for the packet of cluster ions with a size to charge ratio $N'/z = N$ atoms and relative intensity $I(N)$ by expressions (3) and (4) (where C_1 is constant)

$$\frac{dq(N)}{dt} = -q_0U_0^{-1}\frac{dU}{dt} \quad (3)$$

$$\frac{dq(N)}{dt} = \frac{dq(N)}{dN}\frac{dN}{dt} = C_1I(N)t \quad (4)$$

Taking into account the equation of motion of a cluster ion of the effective size N atoms (M_0 is the atomic mass of carbon) in the electric field of a capacitor from ground target plate to accelerating grid (collector) placed at a distance l apart, we obtain

$$x(t) = \frac{eU_0}{(lM_0)}\frac{t^2}{N} \quad (5)$$

Combining (3) and (4), we obtain the resulting expression for $I(N)$

$$I(N, t) \approx C_2\frac{1}{t}\frac{dU}{dt} \quad (6)$$

in which C_2 is constant. Equation (6) allows us to estimate the relative intensities of the detected cluster ions by differentiation of the time dependence of pulsed image potential $U(t)$ over its delay regions. Accounting for the dependence (5) of the effective size of the detected monoenergetic cluster ions on the time of their arrival at the extracting/accelerating grid (probe), the $I(N, t)$ function describes the distribution of cluster ions over their arrival time as in a common time-of-flight mass spectrum.

The composition of the negatively charged products of laser evaporation was studied by the electric probe procedure over the laser power density range of $I_0 = 0.21–1.2$ GW cm^{-2}. Two characteristic groups of cluster ions with size to charge ratio N'/z of 2–20 and 10^4–10^6, respectively, were observed in the mass distribution (Figure 2). To study the processes responsible for the formation of ions in these groups, the angular slopes of ion intensity *versus* laser power density plots were determined using double logarithmic coordinates (Figure 3).

The first group of ions (N'/z 2–20) over the range $I_0 = 0.27$–0.4 GW cm^{-2} (lower than the threshold laser power density value for spinodal decomposition of the labile liquid phase of carbon[6]) is characterised by the slope of 6.0±0.5 (Figure 3). This slope is close to the known value (5.6±0.1)[11] for the yield of C_1^+ ion predominant in the mass spectra of

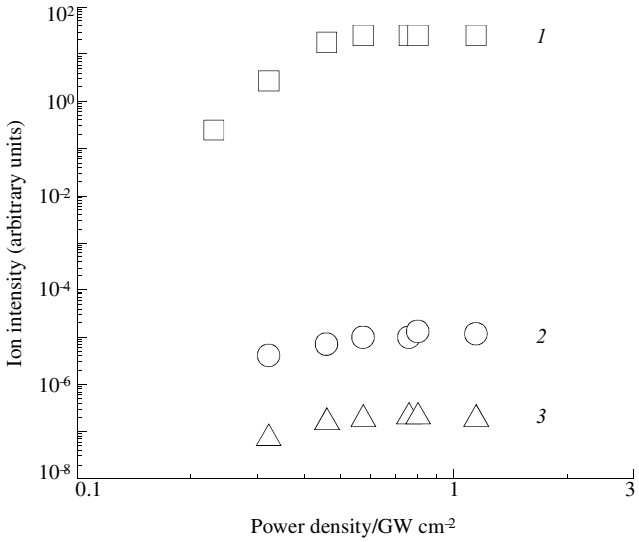

Figure 3 Ion intensity *versus* laser power density plot [N'/z ratio: (*1*) 2; (*2*) 10^4 and (*3*) 2×10^5].

primary carbon cluster ions over the indicated I_0 range. Thus, the observed correlation of the slope values for the yield of C_1^+ and this group of ions explains the formation of this group by the recombination of C_1^+ ions and condensation of neutral carbon atoms followed by the capture of an electron by the cluster formed (electron affinity for the C_2^- particle reaches 3.4 eV[12] and increases as the cluster size further increases), and so the step of formation of the primary C_1^+ ion is limiting.

The second group of negative ions with an N'/z ratio of 10^4–10^6 was observed at power densities higher than 0.33±0.11 GW cm^{-2}, which coincides with the threshold laser power density value for the spinodal decomposition of carbon.[6] It was found that the relative intensities for both groups of ions (small and large) differed dramatically (0.1–10 and 10^{-7}–10^{-5}, respectively) but the total amount of evaporated substance which is estimated as the relative cluster intensity multiplied by N'/z was comparable for both groups of ions. The slope value for the yield of these ions (for example, for cluster ions with $N'/z = 10^4$ and $N'/z = 2\times10^5$) was 1.0±0.1, indicating the similarity of the microscopic mechanism of the ion yield and the macroscopic mechanism of laser-induced mass removal[6] (at power density values higher than 0.3–0.4 GW cm^{-2}). Thus large carbon cluster ions detected seem to be spinodal decomposition products of labile carbon liquid phase.

The saturation of ion intensities for both groups was observed as the laser power density increased in the range 0.5–1.0 GW cm^{-2} (higher than the threshold laser power density value 0.3–0.4 GW cm^{-2} for the spinodal decomposition process for the laser-induced labile liquid phase of carbon) (Figures 2 and 3). Also taking into consideration the saturation of the crater depth plot in the I_0 range[6] (characterising the overall amount of substance evaporated per laser pulse) this phenomenon can be related to laser heating of the spinodal decomposition products resulting in their dissociation and ionisation (Figure 2) and to a change in the form of the initial high mass cluster distribution.

Thus, in this work large cluster (nanocluster) ions of carbon with size to charge ratio (N'/z) up to 10^6 and relative intensities up to ppm (as compared with the same values for small cluster ions with N'/z = 2–20) were detected with a new electric probe procedure. The high sensitivity of the probe procedure was related to the high ion-electron conversion efficiency of probe detection and measurement of the integral image potential induced by the total charge of negatively charged species at the laser plume of carbon.

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