

ENTHALPY-DEPENDENT SIZE DISTRIBUTIONS OF CARBON NANOCCLUSERS PRODUCED BY LASER ABLATION OF GRAPHITE

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Introduction

It is well-known phenomenon of the clustering (spinodal decomposition) of a thermodynamically unstable (labile) liquid phase with near-critical parameters [1]. The characteristic size of droplets formed during the clustering process changes as $R \sim T^{-2/3}$ beginning with the critical temperature of a substance [2]. Meanwhile this phenomenon has not been studied experimentally.

Experimental

Carbon nanoclusters were produced by laser ablation from a low-density graphite foil ($\rho \geq \rho_{\text{crit}}$, where the critical carbon density $\rho_{\text{crit}} = 0.64 \text{ g/cm}^3$ [3]). A sample of the graphite foil was placed on a square linear translation stage moved in the horizontal plane. The surface of the low-density sample was accurately covered with a transparent glass plate to avoid any interface cavities. This glass plate allowed laser irradiation of the target and prevented the removal of the material. The output of a Q-switched Nd:YAG laser (wavelength 532 nm, pulse energy $4.5 \pm 0.3 \text{ mJ}$, pulse width (FWHM) $25 \pm 2 \text{ ns}$, repetition rate $12.5 \pm 0.5 \text{ Hz}$) attenuated by neutral calibrated filters was chopped and focused by a lens through the covering glass plate at the surface of the graphite foil sample with a focal aperture of the laser beam of about $160 \mu\text{m}$. Fresh spots of the sample translated horizontally with a step of $150 \mu\text{m}$ were irradiated by 1-2 laser pulses. Quasi-equilibrium laser evaporation of the subsurface layer of the sample occurred in pores with an average size of 10-20 nm (comparable to a free path length under conditions of intense evaporation) as an isochoric "autoclave" process and was followed by subsequent formation of critical and supercritical states of carbon [4,5] due to a relatively high bulk density of the foil sample. SEM images of the modified surface of the graphite foil irradiated with the laser power densities I_0 0.05, 0.12, 0.3, 0.64 and 1.6 GW/cm^2 were obtained using a commercial SEM instrument (JEM-2000FX with a LaB6 cathode).

During the electrostatic probe experiments a pyrolytic graphite target was evaporated in vacuum by the focused laser radiation at the I_0 range $0.05\text{-}1.5 \text{ GW/cm}^2$. The extracting/accelerating grid of the instrument was used as a collector with the applied constant positive or

negative potentials of 33 V and was placed at a distance of 4 cm from the target at a slight angle ($10\text{-}15^\circ$) to the incident laser beam. Positive and negative carbon cluster ions were detected by the time-of-flight electrostatic probe technique as pulsed image potentials. Multi-charged atomic ions have been detected only for positively-charged carbon species due to intensive electron-ion interactions within a double electrical layer on the front of a carbon plasma. In contrast with the fact negative cluster ions with size N to charge Z ratio up to million atoms have been extracted with a positive potential of the probe. Since large carbon clusters can easily produce multiply-charged cluster ions we have estimated probabilities of yield of multi-charged cluster ions using the microscopic theory of charge density distribution on droplets (mass density fluctuations) of a substance in critical, supercritical or labile liquid states developed [6]. This theory permits to expand non-monotonous image potential dependence on N/Z into a sum of several simple terms which correspond to parent neutral carbon clusters producing series of detected multiply-charged ions. Thus obtained multimodal size distributions of neutral parent clusters were centered at 60, 100, 120, 150, 240, 330, 1000, 4000-8000, 10000 and more (up to million) carbon atoms per cluster (Fig.2). The peak positions N_p of these modes were in a good agreement with the numbers N_c of atoms per multishell spherical fullerenes which were calculated using a scaling law $N_c = (n/b)^3$, where the scaling parameter b equals to 0.3 for spheres and n is the number of shells [7]. The transition from single-shell to double-shell fullerene structure occurs at $N=330$ atoms per cluster and other crossovers with change of n for spherical multishell carbon fullerenes were observed up to $n=25$.

Results and Discussion

Carbon nanoclusters sized from 10 to 40 nm (Fig.1) were observed by SEM on the irradiated spots of the graphite foil surface. The enthalpies deposited in the laser-heated subsurface layer of the graphite foil with thickness $0.1\text{-}5 \mu\text{m}$ depending on the I_0 value ($0.05\text{-}1.6 \text{ GW/cm}^2$) are equal to 600-1200 kJ/mole (Fig.1). These enthalpies are considerably higher than the enthalpy of formation of critical carbon (270 kJ/mole [3]) thus providing support to the conclusions of papers [4,5]

related to generation of a supercritical carbon state at a uncovered surface of the same graphite foil ($\rho \geq \rho_{crit}$) under the same conditions of laser ablation. Therefore these carbon nanoclusters were generated by laser ablation under supercritical conditions when the expanding supercritical fluid of carbon was quenched due to high porosity of the graphite foil and hence exhibited a microstructure of supercritical density fluctuations. The most probable size (diameter) of carbon nanoclusters generated gradually diminishes with increasing the enthalpy deposited in a laser-heated layer of the graphite foil. This tendency is consistent with the current theory of supercritical fluids [1,2] which predicts a temperature-dependent decrease of the correlation radius as $T^{-2/3}$ and thus provides a real opportunity to control the size of laser-generated nanoclusters by choosing proper operation conditions.

Another confirmation of the tendency was obtained by measuring the appearance potentials Be of gas phase parent negative carbon nanocluster ions as slopes of their $\log A - \log I_0$ dependencies multiplied by the laser photon energy (2.33 eV). The appearance potentials of these ions obey the law: $Be = \lambda + Ae - Ea$, where λ , Ea are the enthalpy of formation and the electron affinity of the neutral cluster, Ae is the work function of the liquid carbon. For the large carbon nanoclusters the Ea values were estimated as $Ea(R) = Ae - 0.375 \cdot (e^2/R)$ [8] and then the corresponding λ values were calculated. In the last case we can also find the similar tendency in a decrease of a carbon nanocluster size with the enthalpy growth (Fig.2).

References

- [1]. Skripov VP, Sinitsyn EN, Pavlov PA. *Termodinamicheskie svoystva zhidkostei v metastabil'nom sostoyanii* [Thermodynamic Properties of Liquids in Metastable State]. Moscow: Atomizdat. 1980: C. 1 (in Russian).
- [2]. Prokhorov AM. *Fizicheskaya entsiklopediya* (Physical encyclopaedia). Moscow: Sovetskaya Entsiklopediya. 1990: 353 (in Russian).
- [3]. Glushko VP. *Termodinamicheskie svoystva individual'nykh veshchestv* (Thermodynamic Properties of Individual Substances). Moscow: Nauka. 1979: V.2 (in Russian).
- [4]. Kudryashov SI, Ionov SG, Karabutov AA, Zorov NB. Appearance of the supercritical state of carbon in the laser evaporation of low-density graphite foil. *Mendeleev Commun* 1998: 212.
- [5]. Kudryashov SI, Ionov SG, Karabutov AA, Zorov NB. The role of crystalline defects and density of a graphite foil in the laser-induced degradation. *Mendeleev Commun* 1998: 214.

[6]. Kudryashov SI, Ionov SG, Zorov NB. Microscopic model of charge density distribution for critical and supercritical states of carbon. *Mendeleev Commun* 1999 (in press).

[7]. Tomanek D, Zhong W, Krastev E. Stability of multishell fullerenes. *Phys.Rev.B* 1993; 48(20):15461.

[8]. Haberland H. Clusters, or the transition from molecular to condensed matter physics. Proceedings, NATO Adv. Study Institute on Fundamental Processes of Atomic Dynamics. Italy: Plenum Publishing Corp., 1987.

Acknowledgments

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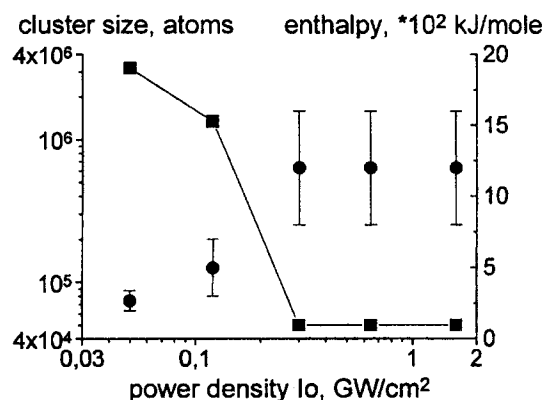


Fig.1. Size of carbon nanoclusters (solid line, dark squares) and deposited enthalpy (dark circles) versus laser power density I_0 .

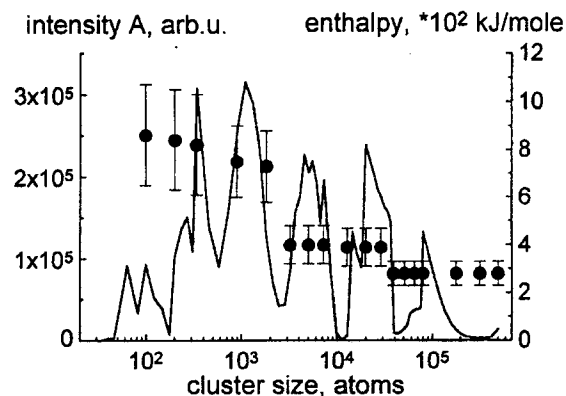


Fig.2. Size dependencies of intensities (solid line) and formation enthalpies (dark circles) of neutral parent carbon nanoclusters.