Homogeneous formation of metastable carbon phases at high degrees of supersaturation

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(Submitted 19 June 1980)
Zh. Eksp. Teor. Fiz. **80**, 413–419 (January 1981)

A thermodynamic confirmation and experimental proof is presented of the production of metastable forms of carbon at high degrees of supersaturation. The experiments were performed by two techniques—with electric discharge and with a laser. Octane, decane, and isooctane were used. Carbon-phase particles measuring up to 20 μm were obtained. Both crystallization methods yielded graphite, diamond, carbynes, and unidentified forms of carbon.

PACS numbers: 81.10.Dn

1. INTRODUCTION

Methods of obtaining and investigating metastable structures of metals, semiconductors, and dielectrics are being intensively studied. One of the methods of obtaining amorphous metals is rapid quenching, which makes it possible to preserve at low temperatures the structure possessed at higher ones.[1] In the carbon system, which has up to ten different phases, quenching methods were successfully used by many workers for the synthesis of diamondlike films.[2-5] In these methods, atomic or ionic beams of carbon are condensed on a cooled substrate. A theoretical calculation based on the analysis of the crystallization in the near-surface layer, has shown that these conditions favor formation of carbon in diamond form.[6] The possibility of nucleation and growth of diamond under these conditions, when it is a metastable form of carbon, was demonstrated in numerous investigations, reported in Ref. 7. It was also shown that at high degrees of supersaturation the orienting action of the substrate on the formation of the new phase ceases to be significant, and this made it possible to obtain diamond films by crystallization on the surface of a metal.[8,9] The possibility was also demonstrated of production of carbyne via heterogeneous crystallization.

In all the investigations performed to date, diamond and other forms of carbon were obtained by crystallization on a surface, i.e., by heterogeneous crystallization. The presence of a surface greatly decreases the work needed to produce the critical seed of the new phase compared with homogeneous nucleation. At the same time there is nothing to forbid in principle the formation of metastable phases in homogeneous crystallization: any of the carbon phases can be produced with some probability or another. Under ordinary conditions of pyrolysis of hydrocarbons, lamblack is produced, in which the basal planes of the graphite are arranged in "cabbage" form. This decreases the surface energy and increases the probability of formation of a critical seed, although under these conditions the stable form of carbon is graphite.

The present paper is devoted to a theoretical confirmation and experimental verification of the production of metastable carbon forms at high degrees of supersaturation.

2. THEORETICAL VERIFICATION

The theory of new-phase formation (nucleation theory) has been rigorously verified for moderate degrees of supersaturation, when the number of atoms or molecules in the critical seed is large enough to be treated macroscopically, and when the work required for its production is large enough. At the same time, an attempt can be made to extend the derivations and formulas of nucleation theory to the region of large degrees of supersaturation. According to papers by Frenkel[11] and by one of us,[12] the rate of homogeneous nucleation, i.e., the number of supercritical seeds produced per unit volume and per unit time can be expressed in the form

$$J=\frac{\alpha P^2}{\rho}\frac{(\sigma m)^{1/2}}{\Theta^2}\exp\left(-\frac{U}{\Theta}\right), \tag{1}$$

where P is the vapor pressure, U is the work of formation of the critical seed, $\Theta=kT$ (k is Boltzmann's constant and T is the absolute temperature), m is the mass of the atom (molecule), ρ is the density of the condensed phase, and α is the condensation coefficient. The nucleation rate at a given P has a maximum at a certain value of Θ which can be found from the condition $(\partial J/\partial\Theta)_P=0$. To simplify the calculations we shall neglect the temperature dependences of the coefficient α and of the condensed-phase density ρ. We neglect also the dependence of σ on the curvature of the seed. We then obtain the equation

$$\left(\frac{\partial U}{\partial\Theta}\right)_P-\frac{U}{\Theta}+2=0. \tag{2}$$

In the classical nucleation theory, the work to produce a critical nucleus is

$$U={}^{16}/{}_{3}\pi\frac{\sigma^3v^2}{\Theta^2\ln^2(P/P_e)}=\frac{B}{\Theta^2\ln^2(P/P_e)}, \tag{3}$$

where P_e is the vapor pressure in equilibrium with the given condensed phase.

In first-order approximation we have

$$P_e=A\exp(-H/\Theta), \tag{4}$$

where H and A (the heat of evaporation and a constant, respectively) are different for different modifications of the condensed phase (e.g., A_1, H_1, A_2, H_2). Differentiating in (3) with allowance for (4) and substituting in (2),

0038-5646/81/010210-04$02.40

we obtain

$$\left(\frac{\partial U}{\partial \Theta}\right)_P=-2\frac{U}{\Theta}-2U\left[\frac{\partial}{\partial \Theta}\ln\left(\ln\frac{P}{A}+\frac{H}{\Theta}\right)\right]. \tag{5}$$

Substituting expression (3) for U and taking (4) into account, we get

$$\frac{U}{\Theta}\left[1-\frac{{}^2/_3H}{\Theta\ln(P/A)+H}\right]={}^2/_3. \tag{6}$$

To calculate the temperature of the nucleation-rate extremum at a given value of P it is necessary to solve Eqs. (6) and (3) simultaneously, and this reduces to an equation of fourth degree in Θ:

$$\Theta\left(\Theta\ln\frac{P}{A}+H\right)^3-\frac{1}{2}B\left(3\Theta\ln\frac{P}{A}+H\right)=0. \tag{7}$$

Since the values of B, A, and H are different for different condensed phases, the temperature of their maximum nucleation rate is also different.

We consider first the particular case $P=A$. In this case supersaturation takes place at all temperatures and approaches zero only as $\Theta\rightarrow\infty$. From (6) we obtain

$$U=2\Theta. \tag{8}$$

It follows then from (4) that at the same time $(\partial U/\partial\Theta)_P=0$. In other words, the maxima of U and J occur at the same temperature, which can be easily obtained from (3)

$$T=\Theta/k={}^8/_3\pi v^2\sigma^3/H^2. \tag{9}$$

The critical-seed radius is obtained from the relation

$$U={}^4/_3\pi r^2\sigma \tag{a}$$

or

$$r=2\sigma v/H. \tag{10}$$

When the ratio P/A increases, the ratio U/Θ corresponding to the extremum of J decreases, but to ascertain whether this growth is monotonic, a special analysis of (7) is necessary, since Θ can decrease simultaneously with the increase of P/A. With decreasing P/A compared with unity, the value of U/Θ increases. Under all conditions, U cannot reverse sign, so that the following inequality must hold:

$$-\Theta\ln(P/A)=\Theta\ln(A/P)<H/3. \tag{11}$$

By virtue of this condition, the value of Θ corresponding to the extremum of J (if this extremum exists) tends to zero as $P/A\rightarrow 0$.

Thus, certain values of the temperature and supersaturation correspond to each of the phases whose production is possible, when the phase nucleation rate is maximal. One can therefore expect a homogeneous formation and subsequent growth of seeds of different metastable phases.

Nucleation in a carbon system at large degrees of supersaturation and at high temperatures can be accompanied by formation of drops of molten carbon, which crystallize into different phases when rapidly cooled. These small particles turn out to be strongly compressed at a Laplace pressure $P=2\sigma_0/r$. Specifying, for example, a value $\sigma=5\times10^3$ erg/cm^2 and $R=10^{-7}$ cm, we obtain $P=60\times10^3$ atm.

It can also be shown that the large surface energy that results from the break of the bonds between the atoms in the molten carbon[13] leads to a substantial change of the lattice parameter a. For a sphere, the relative change is

$$\Delta a/a=2\varkappa\sigma/3r, \tag{b}$$

where $\varkappa$ is the relative measurement compressibility coefficient. For graphite $\varkappa=10^{-11}$ cm^3/erg. For the example given above we then obtain $\Delta a/a=0.2$. This relative change of the lattice parameter is admittedly quite appreciable. It can transform the particle from one crystalline state into another.

3. EXPERIMENTAL PROCEDURE

The experiments were performed in two versions, using electric discharge and a laser. In the electric-discharge method the crystallization took place in the plasma of an electric discharge in a hydrocarbon (octane, decane, dodecane) vapor. Two graphite electrodes were inserted in a Plexiglas cell, into which the liquid hydrocarbon was poured. A high voltage discharge produced the breakdown in the gap. A coincidence circuit made it possible to discharge, following the high-voltage breakdown, a capacitor bank charged to 300 V. The energy of the main discharge was 50 J and the discharge time was 10^{-2} sec. The preliminary high-voltage discharge had too low an energy to affect the liquid. The experiments have shown that hardly any solid particles were produced by the high-voltage breakdown. Following the main discharge, the entire liquid turned black because of the mass precipitation of solid particles, which were investigated after evaporating the liquid. When graphite was used as the electrode material, the bulk of the particles produced in the liquid came from the disintegration of the electrodes. To reduce the influence of electrode disintegration, nickel electrodes were used. In that case, the nickel particles (which were for the most part strictly spherical) were removed with a magnet after the experiments. As a result, the synthesis products remaining in the pulse discharge plasma were burned in air without a residue.

The separated synthesis products were investigated by electron-beam and x-ray diffraction. The diamonds were rid of non-diamond carbon forms by gas etching in a glow discharge.[14] The method is based on the fact that at room temperature the rate of gasification of graphite exceeds that of diamond by 4–5 orders of magnitude.[14] X-ray diffraction revealed in the completely purified powders only diamond and its modification lonsdalite.

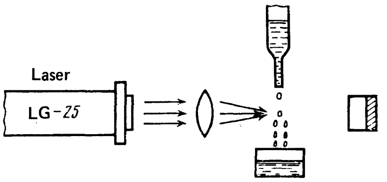

FIG. 1.

Although the different carbon phases were synthesized in the electric-discharge method in the gas phase, the influence of the nickel or graphite surface could not be completely ruled out. A set of experiments was therefore performed on synthesis by laser heating. The experimental setup is shown in Fig. 1. The beam of an LG-25 cw IR laser was focused by a sodium-chloride lens on a falling hydrocarbon drop. The liquid hydrocarbons (the same as used in the electric-discharge method) were placed in a burette with a capillary at the end. By varying the height from which the drop fell from the opening of the capillary to the focus of the lens it was possible to vary the time of action of the laser beam on the drop. The drop diameter was determined by the capillary diameter. The drop repetition frequency was set by varying the air pressure in the burette.

Upon encounter with the laser beam, the drop evaporated intensely, and the radiation was absorbed in the hydrocarbon vapor. At an irradiance exceeding 1500 W/cm^2, a spark was observed. As a result, an aerosol containing both liquid and solid particles was produced around the drop. Part of the synthesis products was dragged by the falling drop and was gathered. The samples for the structural investigations were selected either directly from the aerosol on previously prepared amorphous carbon substrates, or from the liquid residue. When the selection was from the aerosol, an electron microscope revealed individual particles, but they were frequently coated by a high-molecular film, making the electron-diffraction measurements possible. This film was dissolved in the initial hydrocarbon, but aggregates of individual particles were produced.[1)]

RESULTS AND DISCUSSION

Electron-microscope investigations have shown that carbon-phase particles up to 20 μm in size are produced. One cannot rule out, however, the coalescence of individual particles. Tests for polishing ability of a particle suspension obtained by the electric-discharge method has shown that it can polish a hard alloy to approximately class-11 finish.

The particles vary in shape, from irregular to strictly spherical, as shown in Fig. 2. Diffraction investigations have shown that graphite, diamond, carbynes, and unidentified carbon forms are produced in both methods.

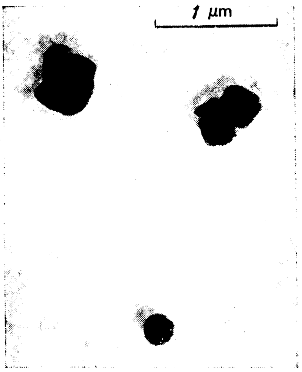

FIG. 2.

TABLE I. Calculation of electron- and x-ray-diffraction patterns of the synthesis products obtained by the electric-discharge method. Distances between planes, Å.

Electron diffr. patt.		X-ray diffr. patt.		Identification
I	II	rel. intensity	d, Å	
4,20	–	–	–	β-carbyne
–	–	10	3,33	graphite
2,55	–	80	2.53	β-carbyne
2,05	2,07	100	2,07	diamond
1.47	–	30	1.50	β-carbyne
		30	1.35	β-carbyne
1,26	1.27	30	1.27	diamond
1,08	1.075	20	1,08	diamond
0,89	0,875	40	0,88	diamond

Table I gives the results of calculation of the electron-diffraction patterns of particles obtained by the electric-discharge method. It shows also the results of calculation, by the Debye method, of the x-ray diffraction patterns of the final process after evaporation. When this product is purified, only diamond remains in the residue.

What is noteworthy in this table is that β-carbyne, which is the α carbyne modification produced at high pressures, is registered. The laser method yields, at the same time, particles of the low-pressure α-carbyne. Figure 3 shows a single-crystal pattern of electron diffraction from an α-carbyne particle.[10] Analysis of the electron-diffraction pattern shows that the diamond particles are highly stressed and have a block structure, as is attested by the broadening of the reflection.

Most spherical particles were electron-amorphous, but some of them yielded diffraction patterns that showed them to be diamonds with a highly disintegrated structure close to amorphous.

It should be noted that particles belonging to unidentified forms of carbon were registered. Table II shows the calculations for the electron-diffraction pattern of one particle. It shows most reflections typical of the

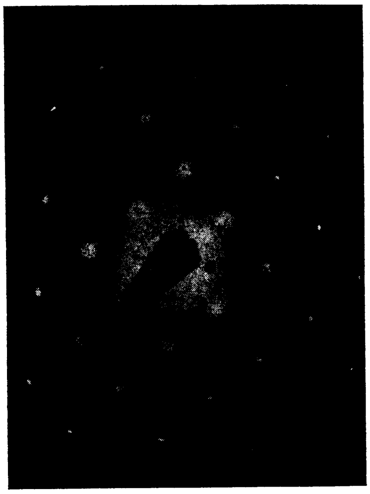

FIG. 3.

TABLE II. Calculation of electron diffraction from carbon particle obtained by laser synthesis. Distances between planes, Å.

Experiment	Hypothetical new phase[15]	Graphite	Experiment	Hypothetical new phase[15]	Graphite
3,02	3,025	3.35	1,47	–	–
2.35	–	–	1.37	1,353	–
2,14	2.139	2.13	1.23	1,235	1,227
1,72	1.746	1.69	1.09	1,114	1,120
1,59	–	–	0.91	–	–
1.53	1.53	1.541			

hypothetical new carbon phase C_8, presumably identified in Ref. 15. The table lists also the data for hexagonal graphite, although some reflections are closer to rhombohedral graphite.

Since various forms of carbon are produced in crystallization at high degrees of supersaturation, a possibility is afforded in principle of searching for still unknown structures. This possibility applies, of course, not only to the carbon system.

The authors thank S. T. Bura for testing the abrasive properties of the synthesis products, and the members of the Sector of Physical Research Methods of their Institute for help with the structural investigations.

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Translated by J. G. Adashko