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Effect of synthesis temperature on hardness of carbon phases prepared from C_{60} and nanosized diamonds under pressure

N.V. Surovtsev [a,*], A.A. Kalinin [b], V.K. Malinovsky [a],
Yu.N. Pal'yanov [b], A.S. Yunoshev [c]

[a] Institute of Automation and Electrometry, Russian Academy of Sciences, Novosibirsk 630090, Russia
[b] Institute of Mineralogy and Petrography, Russian Academy of Sciences, Novosibirsk 630090, Russia
[c] Lavrentyev Institute of Hydrodynamics, Russian Academy of Sciences, Novosibirsk 630090, Russia

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Abstract

Vicker's hardness and Raman scattering spectra have been studied for carbon phases prepared from C_{60} fullerene and nanosized diamonds at high temperatures and a pressure of 6 GPa. It was found that the hardness dependence on annealing temperature has a maximum near ~1100 K for both fullerene and nanosized diamonds as initial materials. This temperature is only slightly higher than the temperature at which the C_{60} cage collapses, and appears to correspond to the termination of intercluster bonding in the case of nanosized diamonds. The hardness maximum is interpreted as a result of competition between an increase in intercluster/intercage bonding and local instability for graphitic-like ordering.

Keywords: Fullerene; High pressure; Raman spectroscopy; Mechanical properties

1. Introduction

Investigations of new carbon phases, synthesized from the fullerite powder under high-temperature and high-pressure conditions, attract significant attention nowadays [1–3]. The phase diagram of the carbon materials and their properties is extremely rich, giving rise to the fundamental topics in this research area. Moreover, the unique features of the carbon phases, which are achievable, define significant interest from applied physics. In some cases, the carbon phases reach very high values of hardness (these phases often called as "hard carbon"), which are combined with a very high plasticity of these materials [3–6]. A critical region of the phase diagram close to the temperature, at which fullerene cages are destroyed, is especially interesting (see, for example, the phase diagram in [3,7]). Some of carbon phases, synthesized in this region, have a ferromagnetism behavior [8–10]. This feature is found for the phases, prepared at pressure of 6–9 GPa and $T = 800–1100$ K. It is interesting that according to [11] this region corresponds to a jump in hardness, if the hardness of the carbon phases is considered versus the synthesis temperature. In the work [12] it was found that there is a hardness maximum near the synthesis temperature of ~900 K for samples, prepared at pressure of 9 GPa. In this work, a significant dependence on annealing time at high temperatures was reported. The annealing time was varied from 0.5 min to 30 min. In [12], it was suggested that the hardness maximum is related to an intermediate state with a time-dependent structure. The statement, that the hardness maximum has kinetic origin and is absent for samples well equilibrated at high temperatures, should be checked. Another question—what is a relation between the hardness maximum and the temperature, at which C_{60} cages are destroyed? Is the hardness maximum a specific feature for fullerene molecules, or carbon phases, synthesized from other nanometer structured

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* Corresponding author. Tel.: +7 383 3307978; fax: +7 383 3333863.
E-mail address: lab21@iae.nsk.su (N.V. Surovtsev).

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carbons, like nanosized diamonds, also have a similar maximum? The present study is devoted to these topics.

2. Experiment details

Carbon phases synthesis was realized by a high-pressure apparatus of a "split sphere" type (BARS) [13] and rapid temperature quenching to the ambient value. Pressure calibration was realized as described in [14]. Stabilized modification of ZrO_2 was used as a material for high-pressure cell, being in a shape of a tetragonal prism. A graphite heater was used [14]. Temperature was measured in each experiment with Pt6%Rh/Pt30%Rh thermocouple whose junction was placed in the central part of the cell, just above a sample. The initial material was packed into platinum ampoule and separated from the heater by MgO or CsCl medium. This allowed us to exclude ingress of graphite.

The samples were synthesized from a fullerite powder with C_{60} content not less 99.9% and from nanosized diamonds, extracted and refined from the explosion soot. The initial material was compacted to cylinders of ∅ 7.1 mm and height of 1.7–2.4 mm. Synthesis of carbon phases was realized at $P = 6$ GPa and at $T = 520$, 870, 970, 1070, 1170, and 1470 K. The annealing time was 5 h, which excludes the kinetic effects like described in [12].

Raman scattering spectra of the samples were recorded using a triple spectrograph TriVista 777 from S& I/PiActon and a line 532 nm from a solid-state laser. A multichannel regime by a silicon CCD matrix with a spectral resolution of $\sim 2.5\ \mathrm{cm}^{-1}$ was used. Nominally right angle Raman scattering experiment was carried out at room temperature with a grazing of the laser beam on the surface (about 60° from the normal). The spherical–cylindrical lens was used in order to focus the laser beam of a power 300 mW into a rectangle 10×0.2 mm on the sample surface, being parallel to a spectrometer entrance slit. Such illumination of the samples results to a relatively low pump power density together with a high integral pump intensity. No polarization selection was applied in Raman experiment. Experimental spectra of inelastic light scattering contained a significant photoluminescence background, which in a limited spectral range was considered as a frequency-independent background and was subtracted from the experimental spectra.

The hardness was measured by the standard Vicker's indentation technique. The value of indenter load was 2 N. In order to overcome the difficulty of high elastic recovery, which was typical for our carbon samples, the true indentation surface was estimated through the sizes of diagonals, clearly seen in microscope with crossed polarizations.

3. Experimental results and discussion

Raman spectra of the carbon phases, synthesized from the fullerite powder, are shown in Fig. 1 in a spectral range $1250–1670\ \mathrm{cm}^{-1}$. This spectral range provides the most intense lines and is quite informative for the carbon phase identification [15]. Raman spectra of initial C_{60} material and 2D-polymerized phase is shown in the top of Fig. 1. The maximum temperature, at which the synthesized carbon phase being a 2D-polymer, was ~870 K. According to [7], the 2D-polymer synthesized at 870 K is mainly rhombohedral ($1406\ \mathrm{cm}^{-1}$ line) with a minor content of the tetragonal phase (the group of lines near $1450\ \mathrm{cm}^{-1}$). (Note that according to the previous interpretation of [16], our sample is almost pure rhombohedral.) As it is seen from Fig. 1b, the pentagonal pinch mode (relatively narrow lines in $1400–1500\ \mathrm{cm}^{-1}$ range [15]) or its analogies are absent for samples, synthesized at 970 K or higher temperatures. It means that the fullerene cages are destroyed for these carbon phases. Raman spectra of the carbon phases, synthesized at 1170 K and higher, are similar as for disordered graphite. A peculiarity of Raman spectrum for a phase, synthesized at 970 K, is a relatively narrow line near $\sim 1581\ \mathrm{cm}^{-1}$, which is very close to the crystalline graphite line [15].

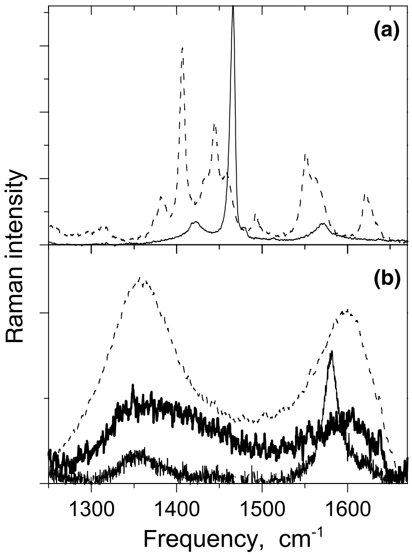

Fig. 1. Raman spectra of carbon phases, synthesized from fullerite C_{60}. (a) Initial material (solid line) and for synthesis temperature 870 K (dashed line). (b) The synthesis temperature 970 K (thin line), 1170 K (thick line), and 1470 K (dashed line).

Presence of the so-called second-order G' band, observed near $2600–2700\ \mathrm{cm}^{-1}$ for green-blue laser excitation, is a common feature to carbon materials, containing condensed aromatic structures ([17] and references therein). The intensity of this band is rather high for a second-order spectrum. Thus, existence of the significant G' band is the evidence that the carbon phase has a graphite-like ordering, resulting in the appearance of aromatic structures. Raman spectra, including the spectral range of G' band, are shown in Fig. 2 (the same intensity scale is used for the lower and higher frequency spectral ranges). The second-order G' band is well seen for Raman spectrum of the sample with the synthesis temperature 970 K and