Effect of high-pressure treatment temperature on the structure of carbon phases formed from C$_{60}$ fullerites under pressure

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Abstract. The synthesis of metal-matrix composite materials reinforced with superelastic hard carbon particles formed from C$_{60}$ fullerites includes heating of the metal-fullerite powder mixture to temperatures above 800°C under pressure. The structure evolution of the carbon particles upon heating from 700 to 800°C at a pressure of 5 GPa has been studied in detail by Raman spectroscopy and indentation hardness measurements. It is shown that the structure of the carbon particle passes the stage of a nanoscale mixture of one- and two-dimensional polymers with the resulting atomic superelastic solid phase. The determining properties of the carbon particles such as superplasticity and high hardness are attained before the complete disappearance of polymerized fullerites, the remnants of which are responsible for the disintegration of the material upon scratching.

1. Introduction
The study of the fullerite transformations upon heating under pressure is important for the search of the production methods for bulk samples of superelastic superhard carbon materials, which now are attainable mostly as thin coatings. It has been established that fcc C$_{60}$ fullerites upon heating from 200 to 800°C at a pressure of not more than 8 GPa undergo two-dimensional polymerization [1]. At temperatures above ~800°C, the C$_{60}$ molecules collapse to the atomic state both under pressure and without applied pressure [2, 3], and this transformation is accompanied by the disappearance of fullerene peaks in the XRD and Raman spectra and the appearance of lines characteristic of amorphous carbon or disordered graphite. The nanoclustered graphene phase (NGP) obtained by the high-pressure high-temperature treatment is characterized by superelasticity and high hardness [4,5]. Such material is advantageous with allowance for its wear resistance and tribological properties, and the particles of a superelastic hard phase obtained from fullerenes under pressure can be used to reinforce metal matrix composite materials. New data on the structure of this carbon material can be obtained by the examination using high-resolution Raman spectrometer CRM 200. The aim of the
work was to trace the sequence of the formation of the superelastic hard carbon phase upon heating at a pressure of 5 GPa.

2. Experimental
Iron-based composite material (CM) samples of 10 mm in diameter and 5-6 mm in height were prepared from a powder mixture of Fe and 10% wt % fullerites C$_{60}$ (99.5%) obtained from the G.A. Razuvaev Institute of Organometallic Chemistry (Nizhny Novgorod, Russia). The CM samples were synthesized with a hydraulic press in standard quasi-hydrostatic high pressure chambers used for the synthesis of superhard materials. The pre-pressed pellet was heated at a pressure of about 5 GPa to 700-800°C and held for 0.5 min. The microstructure of the CM was examined with an Olympus optical microscope. The surface and fractographic features of the carbon particles were examined using a “Quanta 3D FEG” high resolution two-beam scanning electron microscope with a resolution of 1.2 nm. The identification of carbon phases obtained from fullerites under pressure was performed using Raman spectra obtained with a CRM 200 high-resolution Raman microscope at 532.0 nm argon laser excitation in the microsample investigation mode. A Shimadzu dynamic ultra-micro hardness tester at a load of 0.5 N was used to measure indentation hardness (H$_{IT}$), indentation modulus (E$_{IT}$), and elastic recovery ($\eta_{IT} = W_{elast}/W_{total}$, where $W_{elast}$ and $W_{total}$ are the elastic and total indentation works, respectively).

3. Results and discussion
For the study of the fullerite evolution leading to the formation of superelastic hard carbon phase directly on the sample, a temperature gradient of 20 K/mm or 0.02 K/μm was realized over the cross section of the CM sample held for 30 seconds at a temperature of 700-800°C and then this state was quenched. In this case, the particles in the center of the sample remained untransformed, while the superelastic hard carbon phase was formed closer to the edge. The color contrast between the transformed and untransformed particles allowed us to establish the transformation front in the temperature field on the sample polished surface, at which the non-transformed particles look darker (Figure 1).

![Figure 1. Microstructure of the CM obtained from Fe and C$_{60}$ at a pressure of 5 GPa at temperature varied from ~700°C in the center of the sample to ~800°C closer to the edge of the sample.](image-url)
The Raman spectra of the carbon particles corresponding to their positions in the sample are shown in Figure 2. The spectrum taken from a soft black particle, which lies 4000 μm away from the transformation front and exhibits a deep cavity upon indentation, shows that it consists of a mixture of C\textsubscript{60} dimers and polymerized C\textsubscript{60} phases such as one-dimensional orthorhombic phase and two-dimensional rhombohedral and tetragonal phases (Figure 2, line 1).

![Figure 2. Changes in microstructure of the carbon particles in CM from the center to the edge of the sample and the corresponding Raman spectra.](image)

As we trace the particle structure evolution from the center to the edge of the CM sample, that is, as the front of final transformation of the carbon particle to NGP is approached, the intensity of the peaks of two-dimensionally polymerized fullerenes decreases, and the rise of the background line in a range of 1000–1700 cm\(^{-1}\) increases (Figure 2, lines 1 -7). Lines 8 and 9 in Figure 2 are characteristic of the superelastic hard phase, on which there is no trace of scratching by diamond pyramid. Since the Raman spectrum is recorded from a spot of about 1 μm in diameter, we can conclude that the nucleation of the superelastic hard carbon phase occurs in the interior of polymerized fullerite at a submicron level. At the same time, different types of polymers and the superelastic hard carbon phase coexist in a micron volume of the material. A more detailed examination of the Raman spectra shows that the rhombohedral C\textsubscript{60} polymers are most “persistent”. Thus, the structure of fullerite heated to ~800°C at a pressure of 5 GPa is a nanoscale mixture of one- and two-dimensional polymers, as well as the resulting atomic superelastic hard phase. The superelasticity and high hardness are attained by the carbon particles still containing insignificant amount of residual fullerenes. The transformation ends with the complete disappearance of the peaks of polymerized fullerenes. The correspondence of indentation curves to the structure of the carbon parcels is shown in Figure 3.
The polymerized fullerites are characterized by relatively small elastic recovery ($n = 48\%$) at moderate indentation hardness ($H_{IT} = 5$ GPa) and modulus ($E_{IT} = 55$ GPa). In the intermediate state characterized by the presence of retained fullerites, the particle upon microindentation becomes superelastic ($\eta_{IT} = 83\%$), its hardness increases to $H_{IT} = 8$ GPa, but the indentation modulus somewhat decreases to $E_{IT} = 46$ GPa. This is caused by a decrease in the slope of unloading indentation curve as the carbon particle becomes superelastic and the loading-unloading loop becomes narrow. Despite the fact that the particles at the intermediate transformation stage become relatively hard and superelastic, their scratching by diamond pyramid under load leaves a pronounced trace, which can be considered in detail in Figure 4.

A detailed examination of the scratch on the particle, in which the transformation into NGP is not completed and the polymerized structure is retained, shows that the destruction occurs between hard globular “grains”, which are weakly connected to each other. Such hard grains are 20-40 nm size, which corresponds to the average level of the fractal hierarchy of the granular structure of hard carbon [6]. The hard grains are still poorly connected to each other due to the presence of the interlayers of retained fullerites between them. The NGP particle, on which scratching leaves a thin even dent without torn edges is characterized by high hardness ($H_{IT} = 12$ GPa) typical of the C$_{60}$ transformation product at a pressure of 5 GPa, a high elastic recovery ($90\%$), and its indentation modulus reaches 62 GPa. The Raman spectra recorded from superelastic hard particles free from microscopically prominent traces of scratching by diamond pyramid are characterized by a wide unresolvable band typical of amorphous carbon (Figure 2, line 9).
A characteristic feature of the NGP structure is its inheritance link with the deformed structure of the fcc C_{60} fullerite. It is detected both by the relief on the polished surface, which reproduces the slip lines (planes) in fullerite, and by the characteristic deformed fcc structure observed in polarized light in an optical microscope (Figure 5).

![Optical micrographs of the (a) incompletely and (b) completely transformed carbon particles.](image)

**Figure 5.** Optical micrographs of the (a) incompletely and (b) completely transformed carbon particles.

The presence of a picture of a deformed structure in polarized light is another characteristic sign of the NGP formation, since this effect is not detected in the case of the retention of polymerized fullerites in the structure (the center of the particle in Figure 5a).

4. Conclusion
With increasing temperature in a range of 700–800°C at a pressure of 5 GPa, the C_{60} fullerite particles in the metal composite material (CM) undergo changes from a nanoscale mixture of one- and two-dimensional polymers to an atomic nanocluster graphene phase. Such structure changes are accompanied first of all by an increase in indentation hardness and then by an increase in elastic recovery in the presence of an insignificant fraction of retained fullerites. However, even at a sufficiently high level of both characteristics, the scratching of a particle leads to disintegration along the boundaries between nanoscale grains of the hard phase. After the complete disappearance of polymerized fullerites, the carbon particles formed under pressure exhibit superplasticity and high hardness in the absence of noticeable scratches.

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