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Abstract

Comparing the transmission electron microscopy and x-ray diffraction data for a disordered graphite-like (sp^2-bonded) carbon phase (DGCP) synthesized from fullerite C_{60} at high temperatures in the pressure interval from 1.5 to 8 GPa, we show that the nanocluster structure, long-range correlations for orientation of clusters, lamellar and tweed morphology, and possible macroscopic anisotropy are intrinsic properties of the DGCP, and that they can be recognized as a signature of stresses in the parent phase at different scales from the atomic level (atomic density modulation) to the macroscopic one (non-hydrostatic pressure environment). These data indicate that the mechanism of the formation of the DGCP from large-molecule crystalline carbon material, such as C_{60}, is quite uncommon in the standard classification for the first-order phase transitions since it displays features typical for both diffusion and martensitic mechanisms, e.g., a strong topological rearrangement of covalent bonds and a crystallographic-like relation between crystalline parent and disordered product phases, respectively.

The discovery of fullerenes [1] and the production of solid crystalline fullerite C_{60} [2] have greatly stimulated the synthesis of carbon-based materials. Indeed, the application of high pressure and/or high temperatures to C_{60} has provided a means for the synthesis of several ordered and disordered modifications, including crystalline 1D and 2D C_{60} polymers [3–8], a superhard graphite-like (sp^2-bonded) disordered phase [8–12], 3D polymers with a varying degree of polymerization [13–17], diamond-like (sp^3-bonded) amorphous phases [15, 16, 18, 19], and diamond-graphite nanocomposites [15, 16, 20].

The attempts to classify numerous carbon phases prepared from C_{60} under pressure and to systematize their properties can be found in several reviews [21–25], but some of those carbon

phases are of special interest as being potentially promising for practical application [25]. Among them, there is the disordered graphite-like carbon phase (DGCP) [4, 8–12] which combines rather low, typical for graphite, density 1.9–2.3 g cm^{-3} [8–12, 22, 25], very high Vicker's hardness 10–40 GPa [9–11, 22, 24, 25], superelastic recovery [11] and semimetallic resistivity [11, 24]. The relatively low pressures of its synthesis, accessible for today's large-volume high-pressure devices, offer considerable promise for the use of this phase too.

Whereas the mechanisms of polymerization of C_{60} are clear in many respects [3–7, 15, 25], the mechanism of the formation of the superhard DGCP from C_{60} has been much less studied. The structural nature of this superhard graphite-like phase is especially intriguing as specimens of this phase were found to have elastic anisotropy [26–28] and diffusive arc reflections, pointing to a disordered structure with a regular arrangement in reciprocal space [29, 30]. Evident possible similarities of the considered phases to the laser-arc evaporated sp^2-bonded superhard carbon films [31] emphasize the importance of the problems under discussion. One should also note that an understanding of the structural nature and mechanism of the formation of the DGCP can provide further insight into the general problem of superhard carbon phases obtained from fullerites C_{60} [13–16, 22, 24, 25, 32] and C_{70} [33], and of the superelastic recovery of several carbon [11, 31, 32] and carbon-based, such as CN_x [34], materials.

Here we present the systematic study of the DGCP synthesized from fullerite C_{60}, combining x-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. This approach allows us to identify a number of unusual specific properties inherent in this phase, which position the considered material with respect to other disordered carbon phases. The main result of this paper concerns the structural aspects of the formation of the DGCP from polymerized C_{60} molecular structures, since we have shown the nanocluster nature of the DGCP and for the first time have established the existence of structural relations between the parent (C_{60} polymolecular) and the resulting (disordered atomic-based) phase. A new crucial aspect of the present research as compared to the previous structural studies consists of the investigation of partially transformed samples, containing both the parent polymerized C_{60} phase and the product DGCP.

The samples were synthesized from a fullerite powder with C_{60} content of not less than 99.9%. The C_{60} powder was pressed into cylinders of 2–3 mm in height and of 3–4 mm in diameter. Toroid-type chambers [35] were used for generating high pressure and high temperature (0–8 GPa and 600–1400 °C) in a large volume (up to 50 mm^3). The samples were synthesized in almost hydrostatic (NaCl) or non-hydrostatic (graphite) conditions with the outer graphite or Ta heater. The temperature was measured by chromel–alumel thermocouples. The density of the synthesized samples was determined by the bottle method. The structure of the samples was examined by XRD using Cu Kα radiation. The TEM experiments were carried out using JEM-100C and Philips EM430ST (with point-to-point resolution of 0.23 nm) electron microscopes, and the TEM specimens were prepared by diamond powder polishing and, subsequently, by argon ion etching or by cleaving the synthesized samples.

The samples of the DGCP were synthesized on heating to temperatures of about 1000 °C at pressures from 1.5 to 8 GPa (at 1.5, 3, 5, and 8 GPa for the TEM and XRD studies and additionally at 2, 6, and 7 GPa for the XRD). The graphite-like type of bonding of these samples is indirectly evidenced by the XRD data (see the examples below) and by the values of their densities varying in the range from 1.9 to 2.2 g cm^{-3}, depending on the pressure of the synthesis. The recent x-ray photoelectron spectroscopy study has revealed that the DGCP synthesized at 8 GPa has near zero sp^3/sp^2 ratio [36]. In our previous study [10] we showed that there are no significant differences in the density and hardness of the DGCP samples synthesized from 3 to 8 GPa. In the current work we have not detected any considerable differences between the XRD or electron diffraction data (they are considered below) for the
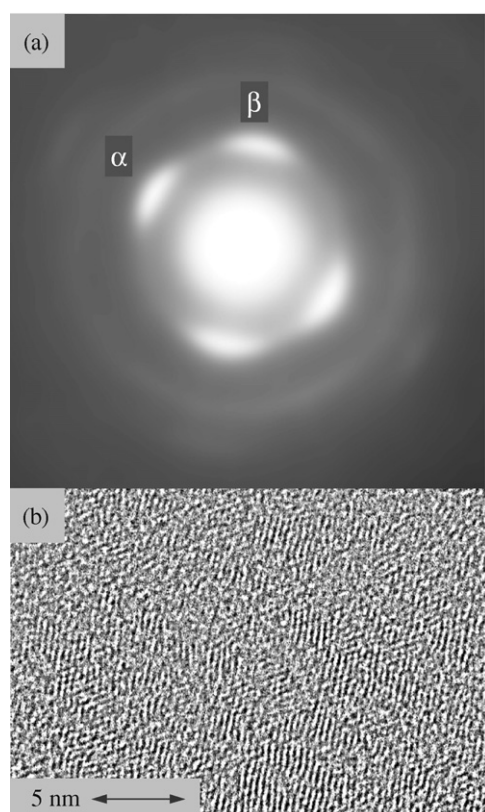
Figure 1. Electron diffraction pattern (a) and high resolution TEM image (b) typical for the DGCP. The synthesis conditions of the sample correspond to 8 GPa and 1000 °C.

DGCP samples synthesized at different pressures from 1.5 to 8 GPa, and one should also add to this set the TEM data for samples synthesized at 9.5 GPa [30].

A typical TEM diffraction pattern for the DGCP is shown in figure 1(a). The observed diffuse arcs indicate, first, the graphitic-type nature of the phase (the reflections correspond to $d \approx 3.4$ Å) and, second, a high degree of atomic disorder. It is clear that there are correlations in orientations of graphite-type planes in the local area of the electron beam. Movement of the beam over the sample shows that these correlations are observed at least along several microns with fixed positions of the diffuse arcs in the diffraction pattern. So, the orientation of the diffraction planes does not change over micron-scale distances, and this clearly indicates the existence of the long-range correlations in orientations of the reflecting graphitic-type planes. Tilting of the sample revealed that the sets of efficiently reflecting planes are parallel to facets of a tetrahedron and there are no alternative reflections (in this respect, see the details of a similar TEM analysis for samples synthesized at 9.5 GPa in [30]). In the general case of an arbitrary orientation of the sample only two diffuse arcs (the α set in figure 1(a)) are visible, and special tilting of the sample is necessary to obtain the four diffuse arcs (the α and β sets in figure 1(a)). One should emphasize that the long-range correlations are a very specific property of the DGCP, distinguishing it from other carbon materials. The observed long-range correlation of reflecting graphitic-type planes with the symmetry of tetrahedron could be considered as a signature of the parent fcc lattice of molecular pristine fullerite C_{60}, but no direct evidences for such a relation have been found so far.
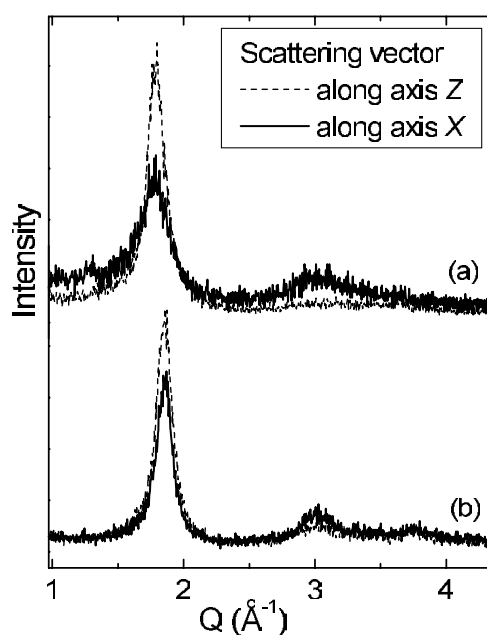
Figure 2. X-ray diffraction patterns (with subtracted middle lines) for the strongly anisotropic (a) and nearly isotropic (b) DGCP, recorded in the 2θ reflection mode for different orientations of the reflecting surface and x-ray scattering vector with respect to the Z axes of the additional uniaxial pressure component. The synthesis conditions correspond to 7 GPa and 1000 °C (a) and to 5 GPa and 1150 °C (b).

The high-resolution electron microscopy data (figure 1(b)) confirm our previous conclusions and are clearly indicative of a cluster nature of the DGCP (here, cluster is in many respects a synonym for nanocrystallite). The typical size of the graphitic-type clusters from figure 1(b) varies between 1.5 and 3 nm, i.e., involves 5–10 atomic layers. The sets of parallel graphene planes clearly differentiate the nanometre scale structure of the DGCP obtained from C_{60} (figure 1(b)) from those of laser-arc evaporated sp^2-bonded carbon films [31] (or sputtered CN_x films [34]). Topologically, this observation is evidence of the domination of six-fold bond rings in graphitic clusters in the DGCP, since such a geometry corresponds to an ideal plane. In turn, this means considerable topological bond rearrangement of covalent bonds during the formation of the DGCP, i.e., the contribution of a diffusion-driven breaking and the formation of covalent bonds.

Another peculiar property of the DGCP, when it is prepared in non-hydrostatic pressure conditions, is macroscopic anisotropy. Primary anisotropy of a synthesis pressure, i.e., the additional uniaxial pressure component, naturally occurs in toroid-type chambers [35] with the non-hydrostatic pressure transmitting media [26]. The discussed macroscopic anisotropy can be evidenced by ultrasonic measurements [26] and XRD (figure 2), when we explore different x-ray diffraction geometries with respect to the axis of synthesis loading, i.e., of the uniaxial symmetry. It is important that the TEM data for anisotropic samples of the DGCP were found to be the similar to those discussed above. The analysis and detailed discussion of anisotropy and the correlation between ultrasonic and structural anisotropy can be found elsewhere [27, 28]. Here, it must be pointed out that anisotropy is a macroscopic property in a microscopically nanoclustered material, and it results from the existence of a predominant orientation of graphite-like clusters with respect to the axes of the uniaxial pressure component [26–28].
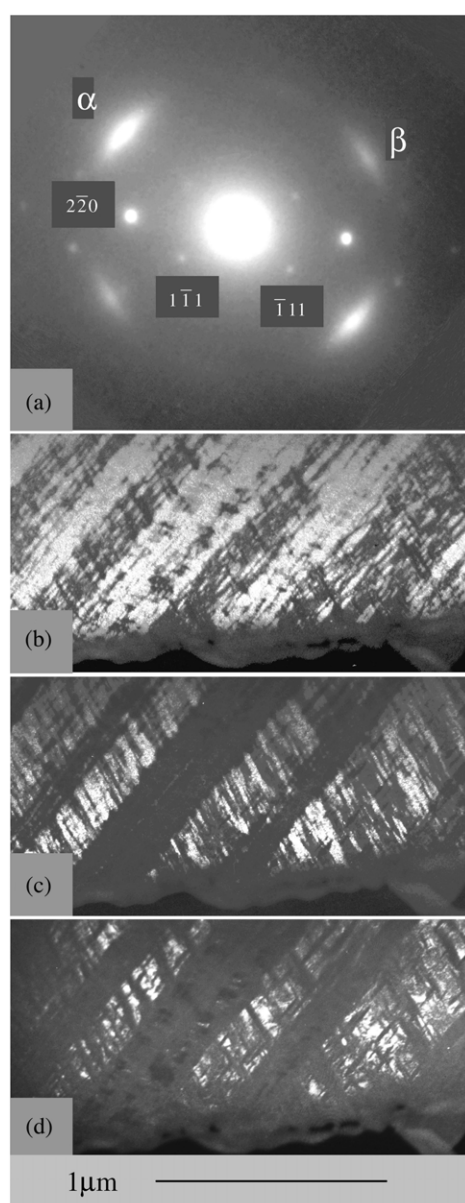
Figure 3. Electron diffraction pattern for the sample corresponding to an intermediate transition stage and containing both the parent molecular C_{60} phase and resulting DGCP (a) and dark field images in the α (b) and β (c) reflections of the DGCP and $(2\bar{2}0)$ reflection (d) of crystalline C_{60} lattice (approximated as fcc of pristine C_{60}). The TEM diffraction pattern of polymerized C_{60} in (a) corresponds to the (110) plane of the reciprocal lattice of the distorted fcc structure. The images (b)–(d) have the same scale and are from the same sample area, corresponding to the single crystallite of the parent C_{60} phase (see the text). The sample was synthesized at 8 GPa and 770 °C.

The key information on the mechanism of the formation of the DGCP has been obtained from the TEM study of the sample corresponding to an intermediate transition stage and containing both the parent molecular C_{60} phase (2D polymerized under the preparation conditions) and the resulting atomic-based DGCP (figure 3). The TEM diffraction pattern

(figure 3(a)) clearly displays the crystallographic-like (the resulting disordered phase cannot have a strictly definite group of symmetry) relation between the parent crystalline and resulting disordered phases. In particular, there is direct correlation in reciprocal space between the α and β diffuse arcs and four crystalline spots. The relative position of the diffuse arcs and the crystalline reflections shows that the graphite-like layers appeared parallel to the close-parked (111)-type planes of the parent fcc or, more exactly, distorted fcc C_{60} phase. The parent phase under synthesis conditions is an intermediate 2D polymerized phase and it can have rhombohedral or tetragonal symmetry [3, 4, 7], but still may be considered as a distorted fcc lattice of close-packed C_{60} molecules.

The TEM dark field images (figure 3(b)–(d)) show that the resulting phase has lamellar and tweed morphology at different scales, and both the parent and the resulting phases are interpenetrative. Here, it is important that the light region in figure 3(d) has the identical orientation of the (220) plane of the C_{60} parent structure, and, so, the observed diffraction patterns (figure 3) were obtained from a single crystallite of the parent polymerized C_{60} phase. The observed lamellar and tweed morphology is typical for the martensitic (displacive) transition [37–39], where the elastic strain accommodation plays an important role. There are also other evidences of the fractal nature of the DGCP and an inhomogeneous structure at different scales [12]. Similar interpenetrative TEM pictures were observed for the preceding 2D polymerized phases [11], probably indicative of a precursor of the current transition picture. On the other hand, here we deal with a high-temperature diffusive transition, taking into account our previous analysis of a high-resolution TEM and the evidence of a strong bond rearrangement. The temperature of the transition to the DGCP, which is nearly independent of the pressure for the interval from 1.5 to 8 GPa [4, 10, 23, 24], points to the diffusive nature of the transition too.

The observed anomalous structural properties can be clearly related to the stresses of different scales. The existence of the predominant orientations of graphite-type clusters, crystallographically related to the parent molecular phase, result from the regular modulation of atomic density and intermolecular stresses in the parent covalent crystalline structure. The interpenetration of differently oriented graphite-like clusters formed during the transition, first, provides a mechanism of relaxation of nanometre scale stresses and, second, results in the nanocluster state. At the same time, the macroscopic elastic stresses directly influence the probability of the formation of differently oriented clusters (for details, see [26–28]). The complicated picture of interpenetrative morphology at the mesoscopic (figure 3) and micrometre [12] scales can be a signature of different stresses which have resulted particularly from the interaction of macroscopic deformation and complicated morphology of the polycrystalline parent polymerized phase [11].

To sum up, one should emphasize the peculiar properties of the DGCP, such as (i) the nanocluster graphite-like structure, (ii) the long-range structural correlations in the cluster orientation, making the DGCP in some respects similar to crystals, but still disordered without translational symmetry, (iii) lamellar and tweed morphology of different scales, and (iv) possible macroscopic anisotropy as the result of the non-hydrostatic synthesis conditions. All these features demonstrate that the atomic-based structure of the DGCP stores information about stresses in the parent molecular phase from the atomic to the macroscopic level. Moreover, this study shows that the transition from the 2D polymers of C_{60} to the DGCP is partially displacive and partially diffusive, providing an example of the phase transition with a complicated displacive–diffusive nature. A similar example of the displacive–diffusive transition was observed for α-GeO_2 in the pressure interval of crossover between diffusive and martensitic mechanisms [39], and there are arguments that such a crossover is quite a general phenomenon for a polymorphism of solids under pressure [39]. Whereas molecular units of

α-GeO_2 are quite simple, fullerite C_{60} has large complicated molecules. A structure consisting of large molecules and strong covalent bonding in molecules seems to be a general precursor for complicated displacive–diffusive transitions at high temperatures under pressure. Still, the role of factors mentioned above for high-temperature atomic rearrangement mechanisms is a subject to be addressed in future studies.

Acknowledgments

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