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PAPER

Transformation-deformation bands in C₆₀ after the treatment in a shear diamond anvil cell

B A Kulnitskiy, V D Blank, V I Levitas, I A Perezzhogin, M Yu Popov, A N Kirichenko and E V Tyukalova

1 Technological Institute for Superhard and Novel Carbon Materials, 142190, 7a Centralnaya, Troitsk, Moscow, Russian Federation
2 Moscow Institute of Physics and Technology State University, 141700, Institutskiy per. 9, Dolgooprudny, Moscow Region, Russian Federation
3 National University of Science and Technology MISiS, 119049, Leninskiy prospekt 4, Moscow, Russian Federation
4 Iowa State University, Departments of Aerospace Engineering, Mechanical Engineering, and Material Science and Engineering, Ames, IA 50011, USA
5 M.V. Lomonosov Moscow State University 119991, Leninskie Gory 1, Moscow, Russian Federation

E-mail: boris@tisnum.ru

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Abstract

The C₆₀ fullerene has been investigated by high-resolution transmission electron microscopy and electron energy loss spectroscopy in a shear diamond anvil cell after applying pressure and shear deformation treatment of fcc phase. Shear transformation-deformation bands are revealed consisting of shear-strain-induced nanocrystals of linearly polymerized fullerene and polytypes, the triclinic, monoclinic, and hcp C₆₀, fragments of amorphous structures, and voids. Consequently, after pressure release, the plastic strain retains five high pressure phases, which is potentially important for their engineering applications. Localized shear deformation initially seems contradictory because high pressure phases of C₆₀ are stronger than the initial low pressure phase. However, this was explained by transformation-induced plasticity during localized phase transformations. It occurs due to a combination of applied stresses and internal stresses from a volume reduction during phase transformations. Localized phase transformations and plastic shear deformation promote each other, which produce positive mechnochemical feedback and cascading transformation-deformation processes. Since the plastic shear in a band is much larger than is expected based on the torsion angle, five phase transformations occur in the same region with no transformation outside the band. The results demonstrate that transformation kinetics cannot be analyzed in terms of prescribed shear, and methods to measure local shear should be developed.

1. Introduction

An intense study of the C₆₀ fullerene structural features began right after its invention [1] when its high mechanical properties were discovered [2, 3]. The indenters made of ultrahard fullerite phases are used in scanning probe microscopy devices. Such phases and related fullerene materials have promising application in production of hard ceramics, since they can be used instead of diamond powders. Unlike other materials which possess from two (zirconium) to several (silicon) high-pressure phases [4], fullerene and carbon are known to have no less than two dozen high-pressure crystalline phases [5–9], including diamond [10] and a variety of amorphous phases. This is caused by the C₆₀ molecule consisting of sixty carbon atoms forming a sphere. The atoms on the sphere are collected in pentagons and hexagons which allow the C₆₀ molecules to connect in various ways resulting in different polymerization.

In this study, we aimed at understanding the processes occurring in C₆₀ under pressure and shear strains at room temperature. For this purpose we used a unique device, the shear diamond anvil cell (SDAC). The application of plastic shear deformations substitutes pressure-induced phase transformations with strain-
induced phase transformations under high pressure [11, 12]. This allows a significant reduction in phase transformation pressure, decrease in the pressure hysteresis of the phase transformations, and may lead to phases not obtained under hydrostatic conditions. Currently, the deformation and transformation mechanisms for strain-induced transformations under high pressure are not thoroughly studied and understood. In particular, the high-resolution transmission electron microscopy (HRTEM) studies have not been reported for C_{60} after pressure and shear treatment. In fact, there are very few HRTEM studies after treatment in a SDAC due to difficulties working with a small, highly distorted sample. A current HRTEM study surprisingly revealed a formation of nanoscale shear bands after compression and shear. This was completely unexpected, because the localized plastic shear deformation requires a softening of material in these regions (thermal softening [13, 14], strain softening [15], transformation softening [16–18], or reaction softening [19, 20]). At the same time, high pressure phases of C_{60} are stronger than the low pressure phase [21]. Phase transformations in C_{60} under pressure and shear are accompanied by the pressure self-multiplication effect [22–24], which is possible for stronger high pressure phases only [11, 12, 16–18]. The HRTEM images for other materials after phase transformations caused by combined pressure and torsion [25–27] do not exhibit any shear banding. The observed results have been explained by transformation-induced plasticity (TRIP) during localized phase transformations, which occurs because of a combination of applied stresses and internal stresses due to a significant volume reduction during phase transformations. Localized phase transformations and plastic shear deformation promote each other producing positive mechanochemical feedback and cascading transformation-deformation processes. Since the plastic shear in a band is much larger than is expected based on the torsion angle, five high pressure phases appear in the same region: linearly polymerized fullerene and polytypes, the triclinic, monoclinic, and hcp C_{60} as well as amorphous structures. Note that these phases can be quenched after thermobaric treatment [5, 6], but here they have been obtained at room temperature and lower pressure. Also, not all of the above phases are strictly identified with our methods, therefore some of them are most probable metastable phases known from thermobaric experiments. No transformation outside the band was observed because the prescribed (averaged) shear strain was not sufficient. These results clarify that transformation kinetics cannot be analyzed in terms of prescribed shear strain, and methods to measure local shear strain have to be developed. The fact that plastic straining allows for keeping five high pressure phases under normal pressure is nontrivial and may be important for engineering applications. Results obtained for C_{60} may lead to the search for similar phenomena in other material systems.

2. Experimental

The C_{60} fullerene purity was better than 99.9% in this study. The initial crystal structure was fcc. We used an experimental setup with SDAC analogous to the one in our previous study [28]. The samples were loaded in a steel gasket without a pressure medium. They were subjected to a shear deformation under load in the SDAC by rotating one of the anvils around the anvil’s symmetry axis. The anvils’ diameter was either 0.39 or 0.6 mm. Altogether, three experiments have been performed. At the first stage, C_{60} samples with an initial thickness of about 20 μm were loaded to pressures of 5, 7, and 11 GPa, respectively. After the shear deformation due to rotation of an anvil by 30°, the pressure was increased to 9, 13, and 15 GPa, respectively, due to a pressure self-multiplication effect, which accompanies the phase transition [22]. A pressure (more precisely, a normal stress component) distribution in the sample before and after the application of shear deformation have been measured using principles of piezospectroscopy [29], i.e., stress-induced shifts of Raman spectra from the diamond anvil. The normal stress was measured along a cross-section of the sample with a step of 10 μm. C_{60} fullerene specimens after the pressure and shear deformation treatment in a SDAC have been investigated by HRTEM. A HRTEM study was performed using a JEM 2010 high-resolution microscope with an electron energy loss spectroscopy (EELS) attachment. The specimen was extruded by the needle from the gasket on the slide plate, broken into fragments, and then deposited on the grid.

3. Results and discussion

There was a distinctive feature of all of these structures: shear transformation-deformation bands. We observed alternating parallel stripes of dark (thicker regions, crests) and light (thinner regions, valleys) tones. At some locations, two systems of bands intersected at different angles (figure 1). We observed no such bands in the initial material. We analyzed crystal structure fragments located both in the crests and in the valleys. The average spacing between such bands varied from sample to sample within the range of 10–50 nm. Figure 2 illustrates the EELS spectra of the sample. As it is already known, the small peak at 287 eV corresponds to the molecular crystalline nature of C_{60} [30]. This indicates that C_{60} molecules are preserved in the sample. Figure 3 shows the C_{60} crystal structure (a) located in the thinner part of the crystal (valley) and the corresponding Fourier
Figure 1. Two systems of deformation bands in C_{60} after shear deformation and high pressure treatment.

Figure 2. EELS spectra of C_{60} after pressure-shear treatment in the shear diamond anvil cell.

Figure 3. Stacking faults and polytypes in C_{60} crystal with the parameter $a_0 = 1.35$ nm, formed in a thin part of a shear band (valley) (a) and the corresponding Fourier transform (b).
transform (b). Some satellite spots can be seen in the latter. This effect results from an atomic layer disorder in the crystal lattice and the absence of periodicity in the given direction, for which neither an ABAB (like in the hcp-lattice) nor an ABCABC (like in the fcc-lattice) sequence exists. Such a structure is probably a polytype.

Figure 4 shows the image (a) of the structure of the fragments in the valleys and the corresponding Fourier transform (b). It can be seen that the fcc lattice is subjected to transformation strains to the different phases in the different areas of the sample (the reflection spots are rather diffuse). Furthermore, some discontinuities are clearly visible in the image. This Fourier transform corresponds to the hcp-lattice of fullerene. The zone axis is [001]. This is evidenced by the symmetry of the spots and the angles between them (close to 60°), because such a cross-section is absent in fcc lattice.

The total amount of investigated fragments was 28: 16 in the valleys and 12 in the crests. It should be emphasized that with a single cross section (as shown in figures 3 and 4), it is difficult to fully recognize the crystal lattice. Therefore, the subsequent arguments are estimates. Our analysis of the crystals has shown that both the crests and valleys consist of differently transformed fcc-lattices. The average crystal parameter in the valleys is 1.337 ± 0.024 nm, it varies from 1.31 to 1.35 nm. In this case, the lattice is slightly distorted, disordered (there are streaks instead of reflection spots), and in some places bands contain amorphous fragments. The average crystal parameter in the crests is slightly larger and is equal to 1.352 ± 0.016 nm. In few cases we found a C_{60} hcp-lattice in the valley. In the valleys, we frequently observed distortions (transformation strains), defects, and fragments of amorphous structures. Sometimes a single structure could be traced passing through several valleys and crests, but differently distorted (figure 4).

A previously performed analysis of a large data set [5, 6] showed that under thermobaric treatment the initial C_{60} fcc-structure is transformed to several non-cubic lattices with different transformation strains. Angles in such lattices differ from 90° by no more than 5° to 6°. It is easy to demonstrate that by changing the angle of the initial C_{60} fcc-lattice within these limits, we can change the angle between the {111} planes by no more than 2°. In the case of 1D-polymerization (C_{60} molecules bond in a chain in one of the ⟨110⟩ directions), a distorted fcc lattice is formed, and its parameter is approximately 1.31 nm. In the case of 2-D polymerization, an approximate fcc-lattice parameter will be equal to 1.27 nm.

According to our data, in the valleys between the crests there were four different crystalline transformed structures with an approximate parameter of 1.31 nm or less, while in the crests there were no such structures. We have not observed the 1.272 nm lattice parameter either. Thus, we can conclude that a more distorted structure is in the valleys than the crests. In some locations, the crystals are likely to have been 1D-polymerized, whereas no 2D-polymerization in the samples is observed.

Shear bands (i.e., regions in which inelastic shear deformation significantly localizes and exceeds the deformation in the surrounding material) are broadly observed in all types of materials (metals [14, 31], rocks, ceramics [20, 32], ionic crystals, organic compounds and polymers [33], polycrystalline alloys [23, 31, 34, 35], and metallic glasses [36, 37]). This is an important mode of inelastic response of the material to mechanical loading, which is observed under static and dynamic loadings, and under single monotonic and cyclic fatigue.

Figure 4. (a) The fragment of a thin part of a shear band (valley) in C_{60} with voids. Crystal lattice of hcp-C_{60}, corresponding to fcc-C_{60} with the parameter a_0 = 1.31 nm. (b) Corresponding Fourier transform.
[34, 35] testing. A necessary condition for the localization of plastic strain is the presence of some softening mechanism, e.g., strain [15], strain rate, or thermal [13, 14] softening. However, main mechanisms of plastic deformations, such as dislocation nucleation and motion and twinning, have not been observed in fullerene, including in the current study. In this case, phase transformations may serve as the deformation mechanism. However, transformation shears for all observed phase transformations of the fcc-lattice are relatively small and cannot accommodate the large shear prescribed by the torsion of an anvil. Amorphization is another transformation-related mechanism of plastic deformation, and the presence of disordered and amorphous phases confirms that this mechanism is active in our study. Strain-induced phase transformations may occur either quasi-homogeneously or in a localized manner. If the product phase is stronger than the parent phase, then deformation is expected to occur quasi-homogeneously. The phase transformations produce regions that are a mixture of the parent and stronger product phases, and further deformation and transformations occur in the weaker parent or less transformed mixture, in which the yield strength is smaller. For fullerene, all high pressure phases are stronger than the low pressure phase [21]. Also, phase transformations in C_{60} under pressure and shear are accompanied by the pressure self-multiplication effect (see [22–24] and here). It is proven analytically [11, 12] and using finite element simulations [16–18] that pressure self-multiplication is possible for stronger high pressure phases only. That is why the shear bands are not expected during phase transformations in fullerene and the quasi-homogeneous deformation and transformations seem logical. Also, HRTEM images for other materials after phase transformation to stronger phases caused by combined pressure and torsion [25–27] do not exhibit any shear banding. In addition, the treatment of the graphite in a SDAC [38] under conditions similar to those in the present study has led to the formation of onions, but without any shear bands. Thus, our observation of the shear bands in fullerene is very surprising and requires theoretical explanation.

The possible resolution of this paradoxical result is in a self-organized cascading interaction between phase transformation and plasticity. Due to the lack of dislocations and twinning and corresponding shear stress relaxation, prescribed large shear initially causes high shear stresses superimposed on high pressure. Crystal–crystal and crystal–amorphous phase transformations initiate at some local stress concentrators, like grain or subgrain boundaries and other structural heterogeneities. Under shear stresses, nuclei accept the shape of plates or ellipsoids with a large aspect ratio aligned in the directions, which produce maximum transformation work during phase transformations. Due to large transformation volume reduction during phase transformations, large internal stresses are generated mostly within transformed regions. In combination with external shear stresses they produce additional plasticity, called TRIP. Thus, even if the strength of the transformed region is larger than in the surrounding, the internal stresses are much larger.

Further, if in the parent phase shear stresses are slightly lower than the yield strength, then parent phase will not deform plastically. At the same time total shear stresses (external plus internal) in the transforming band may reach the larger yield strength of the mixture of the transformed and untransformed phases and produce significant TRIP. This TRIP will be localized in the transformed band until transformation stops (not necessarily completes). The band should contain disordered and amorphized regions because amorphization (disordering) is a part of the main mechanisms of the plastic deformation for fullerene. Traditional plastic deformation due to dislocations and twinning does not change volume. In contrast, amorphization under high pressure is accompanied by volume reduction which in turn produces additional internal stresses. They play a role of positive mechanochemical feedback and can cause further transformations to crystalline high pressure and amorphous phases of fullerene. Thus, an initial transformation causes TRIP which relaxes but produces new internal stresses that cause new phase transformations and TRIP, i.e., this process repeats itself until phase transformation in the band stops. This is rather similar to the cascading mechanism of structural changes formulated in [39, 40]. Strain localization occurs in valleys, and the crests are surrounding perturbed regions where phase transformations do not occur, but some plasticity is possible due to internal and external stresses. The nature of the voids is unclear. They may appear due to large local volume reduction during phase transformations, due to internal stresses during or after pressure release or during sample preparation and will not be discussed here.

Continuum theory for TRIP for different scenarios is presented in [41–43], unrelated to shear bands. Analytical treatment of phase transformations and TRIP in shear is presented in [44] for small strains and [45] for large strains. A similar theory is developed for chemical reactions and reaction-induced plasticity in shear bands in [20]. The main result is in equation

$$\gamma = \varepsilon_0 - \frac{\tau / \tau_y}{\sqrt{1 - (\tau / \tau_y)^2}},$$

which connects TRIP shear, $\gamma$, applied shear stress normalized over the yield strength in shear in the shear band, $\tau / \tau_y$, volumetric transformations strain for phase transformation, $\varepsilon_0$, and concentration of high pressure phase, c. The main point in equation (1) is that TRIP shear occurs at arbitrary applied shear stresses below the yield strength, due to internal shear stresses caused by $\varepsilon_0$. When $\tau / \tau_y$ is close to 1, plastic shear is very large and
theoretically tends to infinity for $\tau/\tau_p \to 1$. However, in our case $\tau/\tau_p < 1$, because $\tau$ is limited by the yield strength in shear of the weaker low-pressure phase. This explains the localization of plastic strain in the transformation/shear band while the non-transformed parent phase is not deformed plastically when shear stresses are below the corresponding yield stress. Note that the TRIP and cascading mechanism of structural changes have been revealed experimentally during phase transformation from hexagonal to superhard wurtzitic BN in SDAC in [39, 40]. However, HRTEM was not performed, so the information about the presence or absence of shear bands is currently unavailable.

4. Conclusions

The C$_{60}$ fullerene was investigated by HRTEM after pressure and shear treatment in a SDAC. It is shown that the samples contain deformation-transformation bands comprising of valleys surrounded by crests with spacing from 10 to 50 nm. The bands consist of crystal fragments with sizes ranging from a few to tens of nanometers. Since plastic shear in a band is much larger than an averaged shear prescribed by a torsion angle of 30°, this leads to five high pressure phases within a nanoscale region: linearly polymerized fullerene and polytypes, the triclinic, monoclinic, and hcp C$_{60}$, as well as amorphous structures. An averaged shear is not large enough to cause phase transformations outside the band. Thus, transformation kinetics cannot be analyzed in terms of prescribed shear strain and methods to measure local shear strain have to be developed. The obtained results demonstrate that plastic straining allows for keeping five high pressure phases under normal pressure. Since high pressure phases of C$_{60}$ are stronger than the initial low pressure phase, localized shear deformation seems contradictory. However, this was explained by TRIP during localized phase transformations, which occurs from a combination of applied stresses and internal stresses due to volume reduction during phase transformations. Localized phase transformations and plastic shear deformation promote each other producing positive mechanochemical feedback and cascading transformation-deformation processes. We plan on considering the origination of the deformation-transformation bands more thoroughly in the future.

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