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# Characteristics of local atomic configurations in ball-milled fullerenes

# Die lokalen Atomkonfigurationen in kugelgemahlenen Fulleren

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Structural changes occurring in C<sub>60</sub> fullerenes after ball-milling processing were studied. The quantitative characteristics of the local atomic configurations were reconstructed by the reverse Monte Carlo method in the structure of pristine and ball-milled fullerenes C<sub>60</sub>, respectively. It is shown that 3-fold atomic rings, indicating complete amorphization of crystalline fullerenes, are dominant in the structure of material after 14 h treatment. The behavior of the distribution of the sphericity coefficient of Voronoi polyhedra validates a gradual structural disordering of molecular crystal of C<sub>60</sub> and, respectively, the formation of amorphous carbon with randomly arranged close-packed structure after continuous ball-milling treatment.

Keywords: Reverse Monte-Carlo / Fullerenes  $C_{60}$  / Ball-milling treatment / Voronoi polyhedra

**Schlüsselwörter:** Reverse Monte Carlo / Fullerene  $C_{60}$  / Kugelmahlung / Voronoi-Polyeder

## 1 Introduction

Carbon nanomaterials are extensively used in technique, medicine, and in consumer products. Fullerenes are one of the most promising allotropic forms of carbon nanomaterials regarding their practical applications. The positive effects of additives of fullerenes  $C_{60}$  to industrial oils on anti-wear and antifriction properties of friction pairs have been established [1–2]. At these conditions, materials are exposed to high temperatures, pressures and mechanical impacts. There are numerous works devoted to the investigation of the structural state of fullerene  $C_{60}$  under high pressure and temperature, including ballmilling processing [3–14]. However, these studies were carried out without measuring the quantitative characteristics of the local structure in the obtained materials. Based on this, the aim of this work is to establish the parameters of structural changes in the local atomic arrangements of crystalline fullerenes  $C_{60}$  during ball-milled processing in a planetary mill.

## 2 Materials and methods

Fullerenes C<sub>60</sub> (99.5 %) produced in the Joint stock company "Fullerene center" were used as a starting material [15]. According to the specification, amounts of higher fullerenes more than ~0.5 % and traces of solvent (toluene) were not present. The fullerene powder C<sub>60</sub> of about 6.7 g and 15 silicon nitride grinding balls were put into a silicon nitride bowl and milled in argon gas atmosphere in a laboratory planetary ball-mill type Fritsch P-6. The milling times were 1, 3, 8 and 14 h at room temperature, respectively. The rotation speed was 400 min<sup>-1</sup>

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for all experiments, the ratio of the ball weight to the sample weight was to 30:1. The specific energy input has been estimated accordingly to the test-object method for the same conditions that were used in all our experiments and estimated to 2.42 J g<sup>-1</sup> s<sup>-1</sup> [16]. The specific energies transferred to the samples were 8.71, 26.1, 69.7 and 122.0 kJ g<sup>-1</sup> for 1, 3, 8 and 14 h of milling, respectively. The ball-milled powders did not contain impurities according to the chemical analysis.

X-ray diffraction studies were carried out on standard diffractometers with filtered Cu  $K_{\alpha}$  and monochromated Mo  $K_{\alpha}$  radiations in Bragg–Brentano and Debye–Scherrer geometry, respectively. The experimental structure factors (SF) and pair radial distribution functions (RDF) were calculated from X-ray data for a detailed study of structural changes in the ball-milled fullerenes C<sub>60</sub>, by the procedure described in Refs. [17, 18]. The simulations of atomic configurations of fullerenes in the initial state and after ball-milling processing were carried out by reverse Monte Carlo method (RMC) using the RMCPow v. 2.4 and RMCA v. 3.14 software packages [19–21]. All model configurations consist of 6480 carbon atoms placed into a box ( $3 \times 3 \times 3$  unit cells in each direction) with size of L = 42.78 Å. A closest approach of atoms was fixed in the point of intersection of the left slope of the first peak of an experimental RDF with the x-axis to eliminate their inevitable overlap [19]. The cut-off distance between carbon atoms was set to  $r_{C-C} = 1.25$  Å.

#### 3 Results and discussion

X-ray diffraction patterns obtained in Cu K<sub> $\alpha$ </sub> radiation demonstrate the gradual amorphization of the initial sample with increasing milling time, *Fig. 1a*. The complete amorphization of the fullerene lattice occurred after 8 h of ball-milling (BM). A further in-



**Figure 1.** Fragments of X-ray diffractograms (a) and structure factors (b) for fullerene  $C_{60}$  in initial state and after ball-milling (Cu K<sub>a</sub> radiation)

crease of milling time to 14 h led to the formation of amorphous carbon due to the full destruction of the fullerene molecules.

The structure factors and radial distribution functions of carbon atoms in ball-milled fullerenes were calculated from the X-ray patterns obtained with Mo K<sub>a</sub> radiation, Fig. 1b. The structure factor of pristine C<sub>60</sub> is characterized by the presence of three intense peaks at  $q_1 = 0.74$  Å<sup>-1</sup>,  $q_2 = 1.25$  Å<sup>-1</sup> and  $q_3$ = 1.44 Å<sup>-1</sup>. They correspond to crystalline fullerene. The peaks s<sub>2</sub> and s<sub>3</sub> started to expand after 1 h of milling, and they coalesced into a very broad peak after 3 h processing. The structure factor is characterized by presence of a very broad peak at q =1.75 Å<sup>-1</sup> after 14 h treatment which is typical for amorphous carbon [22, 23].

Based on these experimental structure factors, the model atomic configurations of ball-milled fullerenes  $C_{60}$  were generated by the reverse Monte Carlo method. The crystalline lattice of fullerene  $C_{60}$  was used as a starting configuration for all cases. At each iteration, one carbon atom was randomly shifted relativity its position on 0.2 Å. A new atomic configuration was obtained and the pair radial distribution functions g(r), the structure factor A(q) and the coefficient of convergence  $\chi^2$  were calculated by the algorithm described in Ref. [19]. The RMC process was iterated as long as  $\chi^2$  was decreasing. The agreement between the experimental and simulated structure factors indicates the correspondence of the generated atomic configurations to the real structure of the materials, Fig. 1b.

*Figure 2* shows the spatial configuration of atoms generated for  $C_{60}$  after ball-milling for 1 h and 14 h, respectively. With the obtained ensembles, it demonstrates the individual molecules are deformed and displaced from their equilibrium positions after 1 h of grinding, Fig. 2a. The molecules of fullerene  $C_{60}$  are decomposed into separated clusters after 14 h of ball-milling, Fig. 2b.

The bond angles distributions were calculated for simulated atomic configurations using methodology [24], *Fig. 3a.* The plot for the pristine fullerenes  $C_{60}$  is characterized by two separated peaks at 108° and 120° corresponding to pentagons and hexagons, respectively. The distribution for 1 h ball-milled material consists of two broad peaks. The first one is located at the position of that is typical for fullerene  $C_{60}$  and the second low intensive asymmetric maximum is positioned at ~60°. It indicates that the car-



**Figure 2.** Spatial configuration of atoms generated for the  $C_{60}$  after 1 h (a) and 14 h (b) of ball-milling

bon atoms are shifted from their equilibrium positions. The intensity of the peak of fullerenes  $C_{60}$  decreased after 3 h of ball-milling and the one at 60° increases, that is connected with a partial destruction of molecules  $C_{60}$ , Fig. 3a. The distribution had the shape typical for carbon in amorphous state at the further increase of milling time [22, 23].

The disordered structure can be more correctly characterized by the concept of a medium range-order [25]. It extends as to the coordination spheres with the size up to 1.2 nm. The quantitative estimation of the medium-range order was performed according to S. King's criterion [26]. It allows to identify the typical atomic configurations in a structure of disordered materials. The rings are formed due to the arrangement of the atoms in polygons with a limited length of the chemical bond. A ring size n of the network is determined by the number of corners in a closed polygon.



Figure 3. Bond angles (a) and ring size (b) (n: number of corners) distributions in the simulated by reverse Monte Carlo atomic configurations for ball-milled fullerenes  $C_{60}$ 

Using S. King's criterion, the ring distributions of carbon atoms for pristine  $C_{60}$  and ball-milled ones are constructed, Fig. 3b. 5- and 6-fold rings are dominant in the structure of pristine fullerenes. The 3-fold rings appeared in addition to 5- and 6-fold ones after 1 h of ball-milling. The number of 3-fold rings increases with the following decrease of the percentage of 5- and 6-fold rings after 3 h of ball-milling. 3-fold rings dominate in the carbon material, indicating the amorphization of fullerenes  $C_{60}$  after 8 h processing.

The local atomic arrangements in the simulated ensembles were examined by Voronoi diagram analysis using a software package [27, 28]. A simulated atomic space was divided into Voronoi polyhedra (VP). An individual VP is a structural unit of the amorphous state that is similar to the Wigner–Seitz cell for crystalline materials [29]. Metrical and topological characteristics of VP are calculated for all studied materials. It was shown that the coefficient of sphericity of Voronoi polyhedral,  $K_{sph} = 36\pi V^2/S^3$  (V and S are polyhedral volume and area, respectively [29, 30]), is the most informative parameter of the topological order in disordered materials [22, 23, 31].

Figure 4 shows the distributions of the sphericity coefficient calculated for the fullerenes  $C_{60}$  after ball-milling. It is found that there is a continuous process of fullerene  $C_{60}$  transformation from crystalline state to the disordered carbon material. A molecular crystal of  $C_{60}$  is characterized by three types of Voronoi polyhedra with the sphericity coefficients 0.3, 0.347, and 0.351, respectively. The sphericity coefficient is characterized by a broad distribution that is decomposed on four components after 1 h ball-milling, *Table 1*. The first broad sub-peak is linked to the fullerene-like component. Its broadening indicates a weak deformation of the molecular crystal  $C_{60}$ . The third maximum takes the position of the disordered tetrahedral network that is typical for 82

Material	Graphite	Diamond	C <sub>60</sub>				
Ball-milling time	0 h	0 h	0 h	1 h	3 h	8 h	14 h
K <sub>sph</sub>	0.35 0.37	0.47	0.30 0.347 0.351	0.38 0.44 0.49 0.55	0.37 0.42 0.48 0.56	0.41 0.49 0.58	0.49 0.58

**Table 1.** Peak positions of the sphericity coefficients of Voronoi polyhedra  $K_{sph}$  of graphite, diamond, and ball-milled fullerenes  $C_{60}$  calculated for model atomic configurations

distorted diamond (0.47). The second peak occupies the intermediate position between graphite and diamond. The fourth small peak appears in the position of the system of random points (0.53) typical for a disordered arrangement of atoms.

 $K_{sph}$  remains visually unchanged, and there is a redistribution of intensities of its sub-components, indicating a partial destruction of molecules  $C_{60}$  after 3 h of ball-milling. Further ball-milling leads to the disappearance of any fullerene-like component, Fig. 4 (8 h). The second and third peaks are shifted towards to higher values.  $K_{sph}$  is characterized by a bimodal distribution after 14 h of ball-milling. The first maximum takes the position close to the disordered tetrahedral network fitting to diamond-like amorphous carbon. The second peak is at the position of random system of points. Such a behavior of the distribution of sphericity coefficient indicates a gradual structural



Figure 4. Distributions of the sphericity coefficient of Voronoi polyhedra for ball-milled fullerenes  $C_{60}$ 

disorder of the molecular crystal of  $C_{60}$  and the formation of amorphous carbon with randomly arranged close-packed structure after continuous ball-milling treatment.

The stability of the structure of fullerenes at ballmilling processing is important. Apparently, it was shown for the first time by HPLC, UV- and IR-spectroscopy that an increased milling time leads to a polymerization of the pristine fullerene molecules [13]. In turn, this results in an increase of the stability of the molecular crystal due to a formation of covalent bonds between individual molecules. Unfortunately, the specific energy transferred to samples during ball-milling is not indicated in most cases, except for Ref. [32] and it complicates the interpretation of the results from different authors. However, a comparative analysis can be performed using X-ray diffraction data. The diffraction pattern given for 1000 h of grinding in [13] corresponds to our data for the sample after 8 h of treatment (energy input about ~70 kJ g<sup>-1</sup>), Fig. 1a. The initial and intermediate stages of decomposition of the molecular crystal  $C_{60}$  were reported [13]. A further increase of milling time resulted in the destruction of the  $C_{60}$ molecules (energy input ~120 kJ g<sup>-1</sup>) and, respectively, the formation of amorphous carbon similar to ball-milled graphite [22, 32].

Preliminary studies with Raman and IR-spectroscopy have shown the presence of dimers in the structure of the milled material that will be reported in the future. The polymerization of pristine fullerenes was observed not only after ball-milling but also at high temperature and pressure [4, 7, 13, 33]. It should be noted that thermodynamic conditions (short-time pulse pressure and temperature:  $\tau \sim 10^{-8}$  s,  $\Delta P \sim 5$  GPa,  $\Delta T \sim 1000$  K) occurring in the material in a shock contact point due to the collision of the grinding balls in the planetary mill [34] are similar to those used in Refs. [4, 7, 33]. They are reasonable for a polymerization of pristine fullerenes as well as for the appearance of diamond-like components in the obtained amorphous carbon [35].

#### 4 Conclusions

The continuous transition of the crystalline structure of fullerene C<sub>60</sub> into the amorphous state in ballmilling processing was studied by reverse Monte Carlo and by Voronoi tessellation methods for the first time. Quantitative characteristics of the local atomic configurations in the structure of pristine and ball-milled fullerenes C60 were established. It was shown that 3-fold atomic rings indicating complete amorphization of crystalline fullerenes are dominant in the structure of the material after 14 h ballmilling. The distribution of the sphericity coefficient (K<sub>sph</sub>) of Voronoi polyhedra validates the gradual structural disordering of the molecular crystal of  $C_{60}$ and the formation of amorphous carbon with randomly arranged close-packed structure after continuous ball-milling treatment. The sphericity coefficient can be applied for the characterization of allotropic forms of disordered carbon. We propose to use K<sub>sph</sub> as a parameter of the topological order to quantify a disordering degree in amorphous structures.

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