PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **2** No 3, 03NCNN28(4pp) (2013)

Structure Transformation in Fullerenes C_{60} at High Temperature Treatment

A.D. Rud[1*], I.M. Kiryan[1], R.M. Nikonova[2†], V.I. Lad'yanov[2], N.M. Bilyi[3], M.A. Merzlyakova[2]

[1] *G.V. Kurdyumov Institute for Metal Physics of NASU, 36 Vernadsky blvd., 03142 Kiev, Ukraine*
[2] *Physical-Technical Institute of the UrB of the RAS, 132 Kirova str., 426000 Izhevsk, Russia*
[3] *Taras Shevchenko National University of Kiev, 60 Volodymyrska str., 01601 Kiev, Ukraine*

(Received 15 February 2013; published online 01 September 2013)

The changes in the local structure of the fullerenes C_{60} are studied after high-temperature annealing. Based on the model of atomic configurations obtained by reverse Monte Carlo, the quantitative characteristics of the topological order are founded for the C_{60} in initial state and after annealing. It is shown that the critical temperature of the beginning of the destruction of the structure of molecular lattice of fullerenes is 900° C (30 min). At this temperature, a partial breakage of the fullerene molecules occurs. At temperature of 1600° C, fully breakage of fullerene molecules and formation of amorphous carbon takes place.

Keywords: Structure, Fullerenes, C_{60}, Reverse Monte Carlo, Rings, Bond Angles Distributions.

PACS numbers: 61.48. – c, 81.05.ub, 61.72.Cc

1. INTRODUCTION

Carbon nanomaterials are very promising for practical application. So, a positive effect of fullerene C_{60} additives to industrial lubricants on wear and tribological properties of friction units is found in a wide range of pressures and loads [1-3]. Under these conditions carbon nanomaterials undergo to impact of elevated temperatures. Therefore, the investigation of a stability of fullerenes at high temperatures is of great interest. The impact of high temperature annealing in different environments on structure states of fullerenes C_{60}, C_{70} and their mixes was investigated in a number of works [4-6].

In this paper, we studied the structural changes in local atomic arrangement in the fullerenes C_{60} occurring after high temperature annealing. To investigate the evolution of their structure state experimental (X-ray diffraction, Raman spectroscopy) and modeling (Reverse Monte Carlo) methods were used. Fullerenes C_{60} were produced in Physico-Technical Institute of Ural Branch of RAS by the traditional arc evaporation of graphite electrodes method with following extraction by toluene in a Soxhlet apparatus. Thermal treatment of fullerite C_{60} was carried out in covered graphite crucibles in CO atmosphere in the Tamman furnace at the different temperatures – 900, 950 and 1600 °C during 30 min and at 1600 °C during 120 min.

2. TRANSFORMATION OF STRUCTURE OF FULLERENES C_{60} AT ANNEALING

2.1 Exeperimental results

X-ray study of the structure of fullerenes C_{60} in the initial state and after high-temperature treatment was conducted in Mo K_α-radiation. Structure factors (SF) of fullerenes C_{60} after annealing were calculated using X-ray diagrams (Fig. 1) by procedure described in [7, 8]. The structure factor of the initial sample is characterized by the presence of three strong peaks in positions of $s_1 = 0.75$ Å^{-1}, $s_2 = 1.25$ Å^{-1} and $s_3 = 1.44$ Å^{-1} which are typical for the fullerite C_{60}. After high temperature treatment at 900 °C, lines s_1, s_2 and s_3 are beginning to expand. At the temperature of 950 °C, line s_1 completely disappears and the lines s_2 and s_3 combine into very broad one with the maximum at $s'_2 = 1.5$ Å^{-1}. The appearance of peak s'_2 indicates that a process of breakage of crystal lattice of fullerite C_{60} is practically completed. Raising the temperature to 1600 ºC leads to the formation of amorphous material with graphite-like type of short-range order.

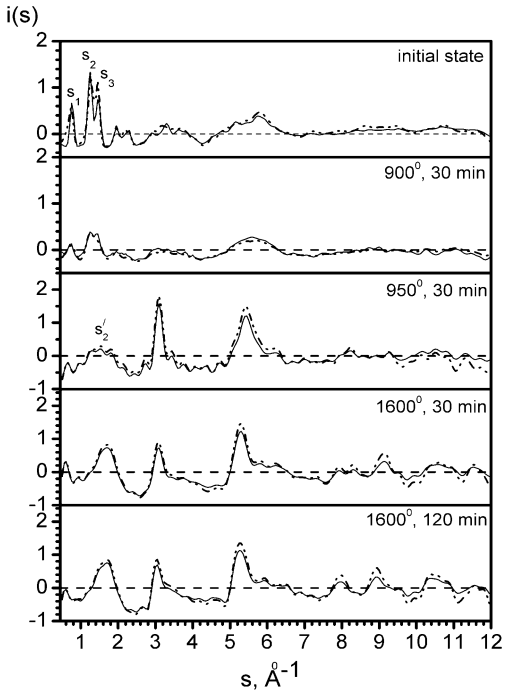

Fig. 1 – Structure factors (-- experimental, ─ calculated) of fullerene C_{60} in the initial state and after high-temperature treatment

* rud@imp.kiev.ua
† RozaMuz@ya.ru

Structural changes in fullerenes C_{60} at the high-temperature annealing were studied by Raman spectroscopy (Fig. 2). This method reproduces the most established information about the structural state of the fullerene molecules [9]. After annealing at the temperature of 900 °C during 30 min Raman spectrum of fullerenes significantly varies from initial one: peaks of fullerenes get broadened and shift from their positions. It indicates a partial breakage of the molecules of fullerenes. Two broad asymmetric peaks on the Raman spectra present with increasing annealing temperature to 950 °C, what testifies to complete destruction of individual bucky-balls. At the temperature of 1600°°C, two bands with maxima at ~ 1345 cm^{-1} and 1600 cm^{-1} which are closed to the positions of the D- and G– bands of disordered graphite, dominate in the spectra (Fig. 2).

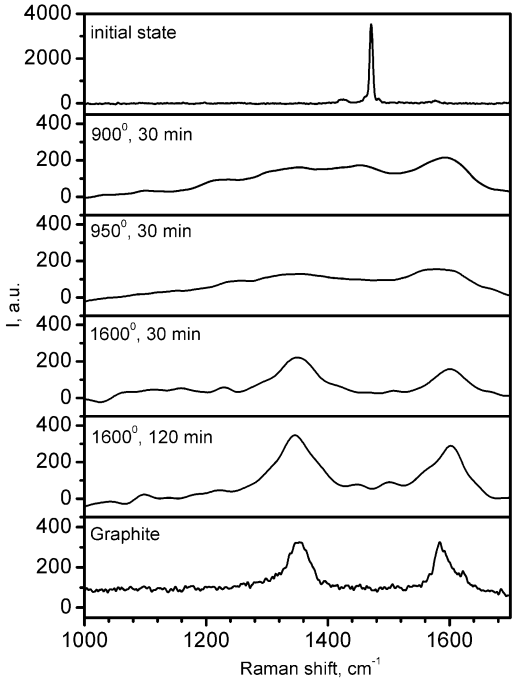

Fig. 2 – Raman spectra ($\lambda = 514$ nm) of the graphite and fullerene C_{60} in the initial state and after high-temperature treatment

2.2 Results of modeling

On the basis of the experimental SF, model configurations of atoms corresponding to the real structure of fullerenes C_{60} in the initial and annealed states were generated using the Reverse Monte Carlo method (RMC) [10]. The cubic simulation box has a half length $L = 21.39$ Å and contains 6696 carbon atoms. Periodic boundary conditions are used. To eliminate the imminent overlap of atoms the intersection of the left slope of the first peak of radial distribution function (RDF) curve g(r) with the abscissa was found. So, the minimal approach of carbon atoms in the model was chosen as $r_{(C\text{-}C)} = 1.2$ Å. Calculated by RMC procedure model structure factors are plotted at the Fig. 1. Accordance of the calculated structure factors (solid lines) to experimental ones (dashed lines) indicates the correspondence of model atomic configuration to real structure of the investigated objects.

Model configurations of carbon atoms in initial C_{60} and annealed at 900 °C (30 min) and 1600 °C (120 min) ones are shown on Fig. 3. It can be seen that process of destruction of molecules C_{60} starts at 900 °C (Fig. 3, b). At a temperature of 1600 °C (Fig. 3, c) molecules of fullerene C_{60} break down into small fragments of deformed graphene planes.

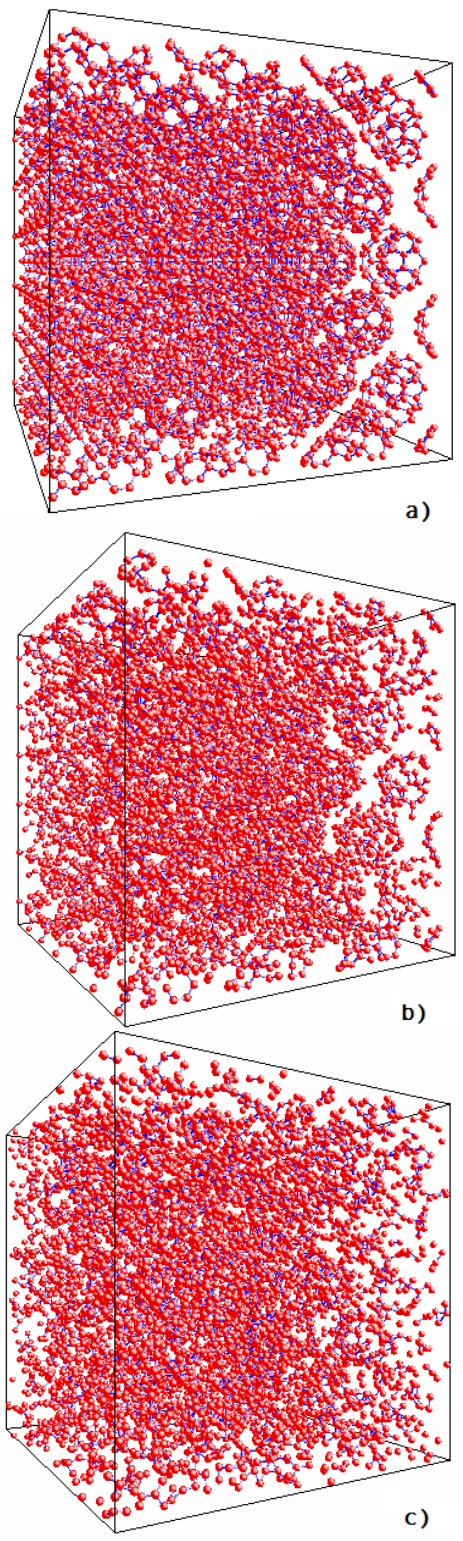

Fig. 3 – The configuration of carbon atoms generated for fullerenes C_{60}: a) initial state; b) 900 °C, 30 min; c) 1600 °C, 120 min

Bond angles distributions were calculated for obtained model atomic configurations of fullerene C_{60} (Fig. 4). It is characterized by a broad maximum which decomposes into two components with the positions of ~110° and ~117° (the table values for fullerene C_{60} are 108° and 120°) for molecules of fullerenes in the initial state. After high temperature treatment at 900 °C for 30 minutes, the typical for fullerene C_{60} peak stays in place, but low intensive broad asymmetric maximum with position of ~60° appears. It indicates that displacements of carbon atoms from balanced position take place in the structure of molecules C_{60} at the annealing process. With increasing temperature to 950 °C, peak peculiar to fullerene C_{60} becomes essentially lower with simultaneous raising the peak at 60°, what suggests the complete destruction of molecules C_{60} and formation of amorphous state in the carbon material.

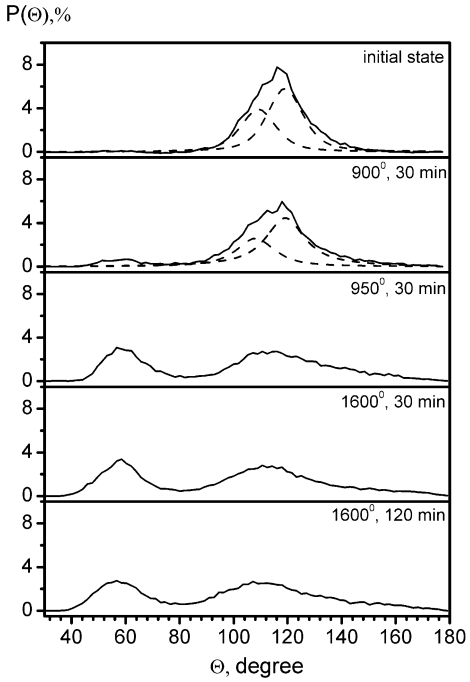

Fig. 4 – The bond angles distribution in carbon atoms configurations in the fullerene C_{60} generated by Reverse Monte Carlo method in the initial state and after high-temperature treatment

Rings distributions (Fig. 5) for the all studied materials were calculated using the criterion of S. King [11]. Rings are formed by connection of atoms within the maximum length of a chemical bond. They define the intermediate range order, which extends not only to the first coordination sphere as it is assumed in definition of short-range order, but to following coordination spheres at a distance of 1-2 nm [12]. Ring size *n* is determined by the number of angles in it.

It is clearly seen, that structure of fullerenes C_{60} in the initial state is characterized by 5- and 6-fold rings which constructed their molecules (Fig. 5). At a temperature of 900 °C, an essential amount of 3-fold rings appears with simultaneous decrease of the percentage of 5- and 6-fold ones. Enhancing the annealing temperature to 950 °C results in increasing the percentage of 3- fold rings what indicates the destruction of the fullerene molecules and formation of amorphous structure. At the 1600 °C reverse changes start to be realized: the percentage of 3-fold rings decreases with simultaneous rising of 5-and 6-fold ones. The amount of 5- and 6-fold rings is growing with extension of expose at this temperature to 120 min, what pointed to partial graphitization process of amorphous material.

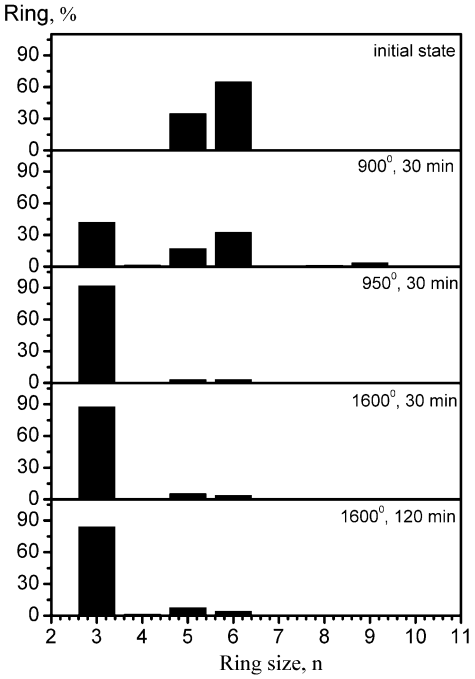

Fig. 5 – Rings size distribution n (n - number of edges) in the structure of fullerenes in the initial state and after high-temperature treatment

3. CONCLUSIONS

Structure transition in fullerene C_{60} from the crystalline state to amorphous during annealing was reconstructed using Reverse Monte Carlo procedure. Quantitative characteristics of topological order in the distribution of carbon atoms were established. It was found that in the early stages of heat treatment (T = 900 °C for 30 min) the partial destruction of C_{60} molecules and disordering the crystal lattice of fullerite C_{60} take place. The annealing at 950 °C for 30 min results in the total breakage of the fullerene molecules followed by the formation of amorphous structure of carbon with graphite-like type of short-range order with increasing temperature to 1600 °C.

AKNOWLEDGEMENTS

This work was partially supported by the joint project of NAS of Ukraine - SB RAS (#03-09-12) and by the Program of the Presidium of the UrB RAS (#12-T-2-1015).

REFERENCES

1. D.G. Tochil'nikov, B.M. Ginzburg. *Technical Physics.* **44**, 700 (1999).
2. B.M. Ginzburg, M.V. Baidakova, O.F. Kireenko, et al. *Technical Physics.* **45**, 1595 (2000).
3. A.I. Komarov, V.I. Komarova, A.D. Rud, et al. *Surface Engineering and Applied Electrochemistry*. **47**, 18 (2011).
4. I. Mochida, M. Egashira, H. Koura et al. *Carbon*. **33**, 1186 (1994).
5. V.I. Lad'yanov, R.M. Nikonova, M.A. Merzlyakova et al. *Perspectivnye Materialy*. **9**, 165 (2010), (in Russian).
6. R.M. Nikonova, M.A. Merzlyakova, V.I. Lad´yanov et al. *Inorganic materials: Applied Research.* **3**, No 1, 44 (2012).
7. A.D. Alekseev, G.M. Zelinskay, A. Ilinskii et al. *Physics and technology of high pressure.* **18**, No3, 35 (2008) (in Russian).
8. A.D. Rud, N.I. Kuskova, L.I. Ivaschuk, L.Z. Boguslavskii and A.E. Perekos, *Synthesis of Carbon Nanomaterials Using High-Voltage Electric Discharge Techniques. in Nanomaterials* (Ed. M.M. Rahman) (Rijeka, Croatia: InTech: 2011)
9. S. Amer. Maher *Raman spectroscopy, fullerenes and nanotechnology*. (USA, Published by the royal society of chemistry: 2010).
10. R.L. McGreevy, L. Pusztai, *Molecular Simulation* **1**, No6, 359 (1988).
11. S. Le Roux, V. Petkov, *J. Appl. Cryst*. **43**, 181 (2010).
12. C.C. Wang, C.H. Wong. *Journal of alloys and compounds.* **509**, 10222 (2011).