

Graphitization and microstructure transformation of nanodiamond to onion-like carbon

Zhijun Qiao^a, Jiajun Li^a, Naiqin Zhao^{a,*}, Chunsheng Shi^a, Philip Nash^b

^a School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China

^b Department of Mechanical, Materials and Aerospace Engineering, Illinois Institute of Technology, Chicago, IL 60616, USA

Received 30 July 2005; accepted 20 September 2005

Available online 20 October 2005

Abstract

Onion-like carbons were synthesized by annealing diamond nanoparticles at 1100–1400 °C. The diamond nanoparticles begin to graphitize in the range of 1100–1200 °C and all the particles transform into onion-like carbons at 1400 °C. The transformation temperature changes with the nanoparticle size. The onion-like carbons exhibit similarity to the original nanoparticles in shape.

© 2005 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Annealing; High-resolution electron microscopy; Microstructure; Onion-like carbons

1. Introduction

The discovery of onion-like carbons has been of great interest from the viewpoints of science and technology [1]. Onion-like carbon consisting of concentric multilayer graphite sheets is one of the fullerenic forms of the new carbon allotropes, and can be produced by many techniques [2–7], such as arc-discharge, irradiation and nanodiamond annealing. The preparation and growth mechanism of onion-like carbons by nanodiamond annealing have been studied extensively because of their wide potential applications in electromagnetic devices, field emission and solid lubricants [8–11].

The quasi-spherical onion is formed by the closure of curved graphite sheets. The transformation is a process of diamond graphitization [12] and starts at a much lower temperature than that of bulk diamond. Bulk diamond graphitizes into planar graphite, whereas nanodiamond transforms into onion-like carbon. The presence of onion-like carbon after the graphitization of nanodiamond makes it both scientifically interesting and technologically impor-

tant to study the transformation from diamond nanoparticles to onion-like carbons [13–16].

Despite the intense interest in the creation of onion-like carbons from diamond nanoparticles, the formation mechanism is not very clear, e.g. how the multishell fullerenes come into being and why the shape of onion-like carbons is diverse. The purpose of this work was to study the graphitization and microstructure transformation of nanodiamond, including graphitization temperature and the resulting shapes of onion-like carbons. We have obtained onion-like carbons by annealing diamond nanoparticles at low temperature and studied the formation mechanism of onion-like structures by X-ray diffraction (XRD) and high-resolution electron microscopy (HREM) analysis. We also propose a model to explain the experimental phenomena in the structure rearrangement of nanodiamond.

2. Experimental procedures

Annealing of diamond nanoparticles (2–10 nm) was performed in a tube furnace in argon atmosphere at temperature from 900 to 1400 °C for 1 h. The nanodiamond samples were placed in a quartz boat and then heated

* Corresponding author. Tel./fax: +86 22 8740 1601.

E-mail address: nqzhao@tju.edu.cn (N. Zhao).

to the annealing temperature at a rate of 10 °C/min. Afterwards the annealed samples were furnace cooled to room temperature under argon atmosphere.

The samples were characterized using XRD to determine crystalline structure and HREM for microstructure observation. The XRD measurements were carried out on a RIGAKU D/Max 2500 diffractometer using Cu K α radiation. For HREM observation, samples were dispersed in ethanol by ultrasonication and then placed on the holey carbon films deposited on copper grids. HREM was carried out on a TECNAI G²F20 microscope at 200 keV with a point resolution of 0.21 nm.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of nanodiamond annealed at different temperature from 900 °C to 1400 °C for 1 h. The diffraction pattern of nanodiamond shows broader peaks at $2\theta = 43.7^\circ$ and 75.1° corresponding to (111)_d and (220)_d diamond planes and no graphite peak can be observed in Fig. 1(a). The diffraction peaks are obviously broadened owing to the very small crystallite size, strains and defects [17].

The XRD patterns of sample (b) and (c) are similar, indicating no obvious change in diamond structure at 900 and 1100 °C. A broad diffraction peak of (002)_g graphite planes at $2\theta = 25.2^\circ$ gradually increases with increasing annealing temperature. The appearance of the broad graphitic (002) peak comes from the onion-like nanographite [18]. The intensity of the (002)_g graphite and (111)_d, (220)_d diamond peaks changes considerably, as shown in Fig. 1(c) and (d), which indicates that onion-like carbons begin to form in the range of 1100–1200 °C. The diffraction pattern for sample (e) shows a significant difference to that

of sample (d). Two graphite peaks corresponding to the (002) and (100) planes at $2\theta = 25.8^\circ, 43.5^\circ$ can be clearly seen and the diamond peaks disappear. It can be concluded that graphitization of nanodiamond finishes after annealing at 1400 °C for 1 h.

3.2. HREM observation

Fig. 2 shows an HREM image of initial diamond nanoparticles 2–10 nm in size. The outlines of the particles are clear and the particles take on diverse shapes. The lattice fringes are obviously seen which correspond to the (111) planes of diamond. The interlayer spacing is 0.206 nm, shown in Fig. 3, which agrees with that of the diamond (111) planes.

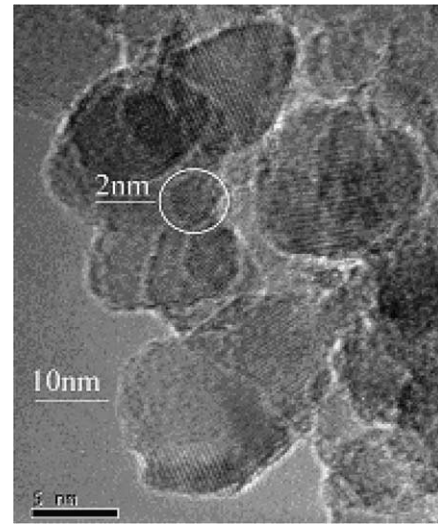


Fig. 2. HREM image of initial diamond nanoparticles.

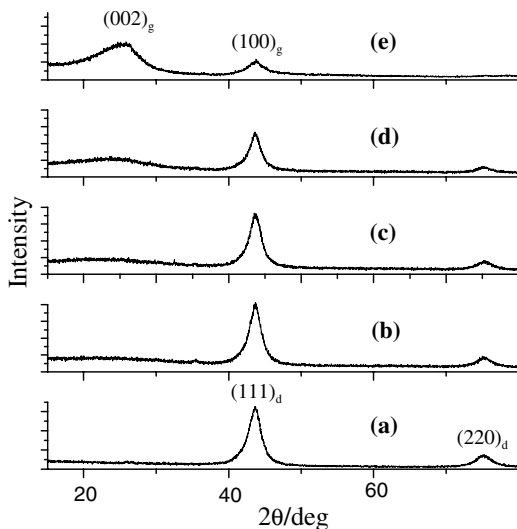


Fig. 1. XRD patterns of diamond nanoparticles annealed at different temperature: (a) diamond nanoparticles; (b) 900 °C; (c) 1100 °C; (d) 1200 °C and (e) 1400 °C for 1 h.

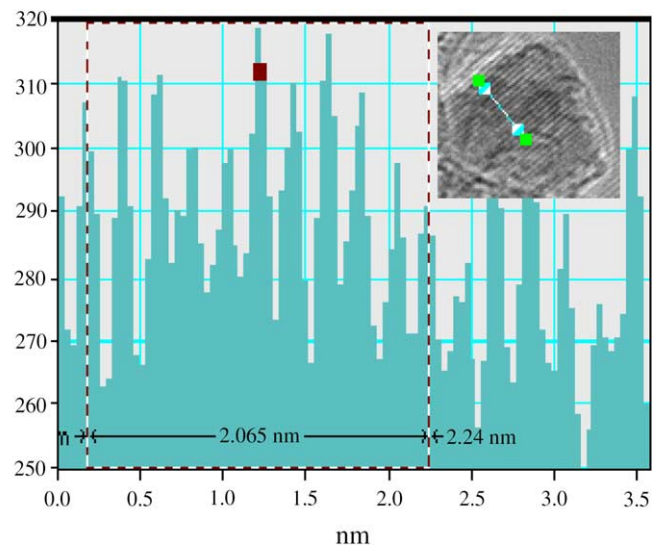


Fig. 3. The interlayer spacing of nanodiamond (111) planes.

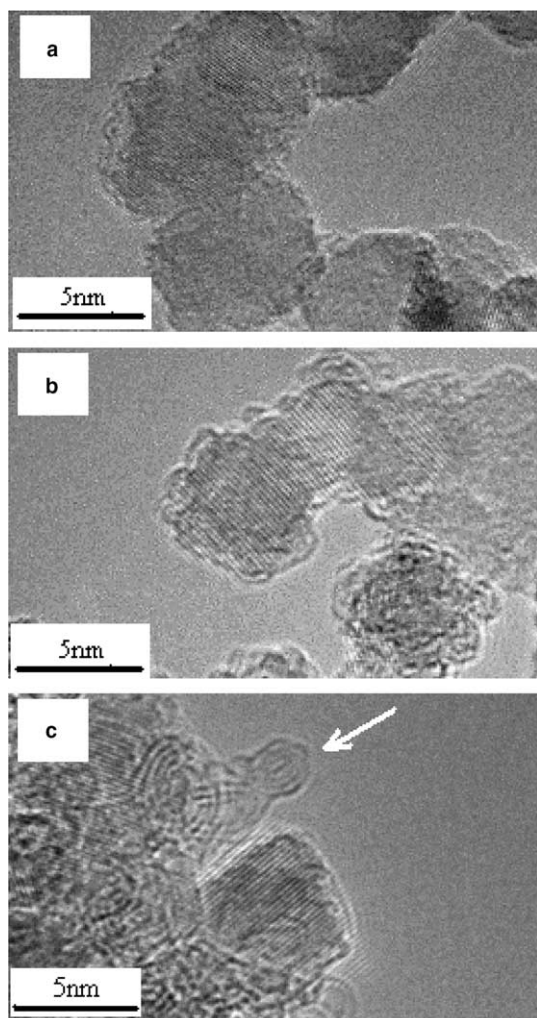


Fig. 4. HREM images of nanodiamonds annealed at (a) 900 °C, (b) 1100 °C and (c) 1200 °C.

Fig. 4(a)–(c) presents the HREM images of nanodiamond annealed at 900, 1100 and 1200 °C, respectively. As seen in Fig. 4(a), the graphite fragments appear at the surface of the nanodiamond annealed at 900 °C. The graphite fragments increase with increasing annealing temperature and gradually connect up into curved graphitic sheets, close to diameters of C_{60} and higher fullerenes (Fig. 4(b)). But no onion-like carbons are found among diamond nanoparticles, which indicates that the inner diamond structure is still stable at 1100 °C. The presence of exterior curved graphitic sheets makes us believe that graphitization of nanodiamonds begins from the particle surface towards the center.

Onion-like carbons can be observed in the HREM image of nanodiamond annealed at 1200 °C, as shown in Fig. 4(c). It can be seen that onion-like carbons coexist with untransformed diamond nanoparticles and the onion-like carbons are smaller in size. It reveals that the graphitization temperature of nanodiamond changes with the degree of crystallinity, in correspondence to particle size. These changes are in agreement with the XRD results that

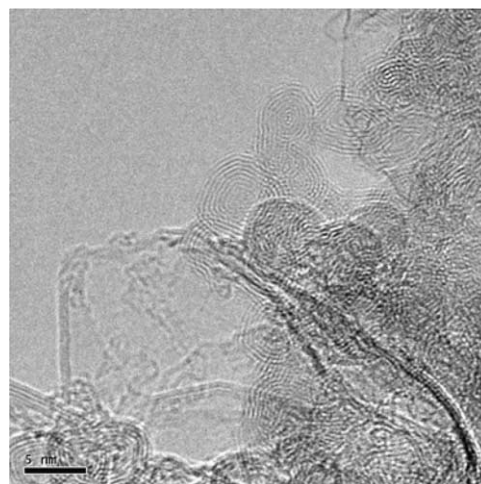


Fig. 5. HREM images of nanodiamond annealed at 1400 °C.

onion-like carbons begin to form in the range of 1100–1200 °C. It should be noted that there exist diamond (111) sheets in the center of the elliptical onion-like carbon (marked by arrow in Fig. 4(c)) and the axis of the elliptical onion-like carbon is parallel to the original diamond (111) planes. We believe that transformation preferentially begins at (111) planes and the inner diamond has an effect on the outer shells in shape. It is reasonable that the onion-like carbons are similar to the original nanoparticles in shape; therefore, we propose that the graphite fragments exfoliating from diamond (111) planes enclose around the surface of nanoparticles gradually and the onion-like carbons develop simultaneously.

Fig. 5 shows an HREM image of diamond nanoparticles annealed at 1400 °C. All the nanoparticles are transformed at 1400 °C and onion-like carbons take diverse shapes, such as quasi-spherical, elliptical, polyhedral and deformed onions. Some onions are found to be enclosed with linked external layers. The number of onion graphitic shells ranges from several to 12.

The interlayer spacing of onion-like carbon with five shells is 0.335 nm, consistent with that of planar graphitic (002) planes; but the interlayer spacing of onion-like carbon with 10 shells is 0.324 nm, smaller than 0.335 nm, as shown in Fig. 6. It can be deduced that the presence of interlayer spacing decrease causes strain between graphitic shells. This conclusion can be explained by the fact that the initial outer graphitic shells restrict the inner transformation in a spherical space.

3.3. Graphitization mechanism

Graphite is the most stable form of carbon at normal temperature and diamond tends to transform to graphite spontaneously at high temperature. Diamond nanoparticles possess more dangling bonds and higher surface energy than bulk diamond due to the high ratio of surface atoms to the total. Consequently, the graphitization temperature

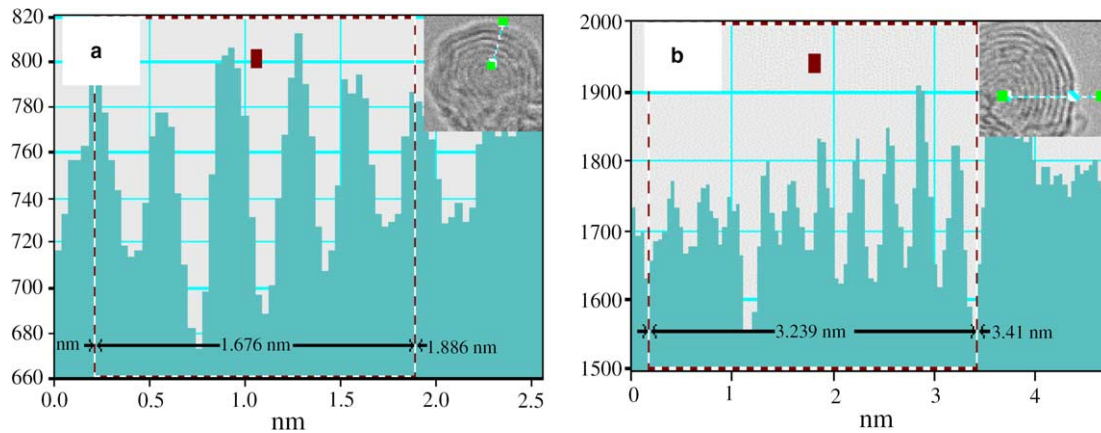


Fig. 6. The interlayer spacing of the graphite (002) planes: (a) five shells and (b) 10 shells.

of nanodiamond is much lower than that of bulk diamond. The elimination of dangling bonds at the nanoparticle surface and the closure of graphite sheets result in the decrease of the surface energy, which is supposed to be the driving force to form closed graphite shells continuously [18].

It has been proved by many researchers that the graphitization preferentially begins at diamond {111} planes [19–22]. There are eight planes in {111} group which comprise (111), ($\bar{1}\bar{1}1$), ($1\bar{1}\bar{1}$), ($1\bar{1}\bar{1}$), ($\bar{1}11$), ($1\bar{1}1$), ($11\bar{1}$) and ($\bar{1}\bar{1}\bar{1}$) planes. The diamond {111} planes are composed of zigzag hexagonal rings that can be easily rearranged into graphite sheet; therefore, graphite fragments with different numbers of carbon atoms exfoliate from the external surface of any diamond {111} plane and surround diamond particles (shown in Fig. 7). These fragments are rearranged by introducing pentagonal and other polygonal rings to form a closed shell. Experimental results show that nanodiamond should be heated to at least 1100–1200 °C for graphitization because enough kinetic energy is required to keep on breaking C–C bonds in inner diamond. But the graphite fragments can form at 900 °C because of the greater number of defects and higher kinetic energy at the outmost surface than in the inner part.

The formation process of onion-like carbons includes: formation of graphite fragments, connection and curvature

of graphite sheets at the edges of diamond {111} planes, closure of graphite layers. Based on the morphological information observed by HREM we propose a model to explain the phenomenon that the onion-like carbon is similar to the original nanoparticles in shape. As shown in Fig. 8, the graphite fragments link and tangle around the surface of the diamond particle to eliminate dangling bonds, and then generate closed graphite shells to diminish surface energy. The inner diamond maintains the original shape and dwindles little by little in the course of transformation. Consequently, graphitic layers enclose around the

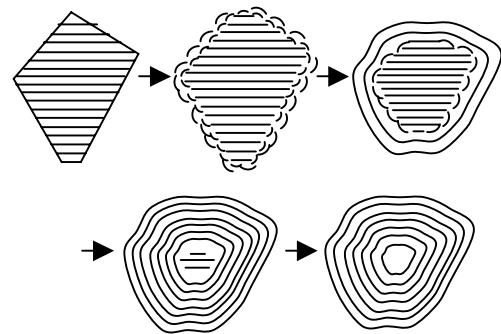


Fig. 8. Schematic illustration of onion-like carbons formation process.

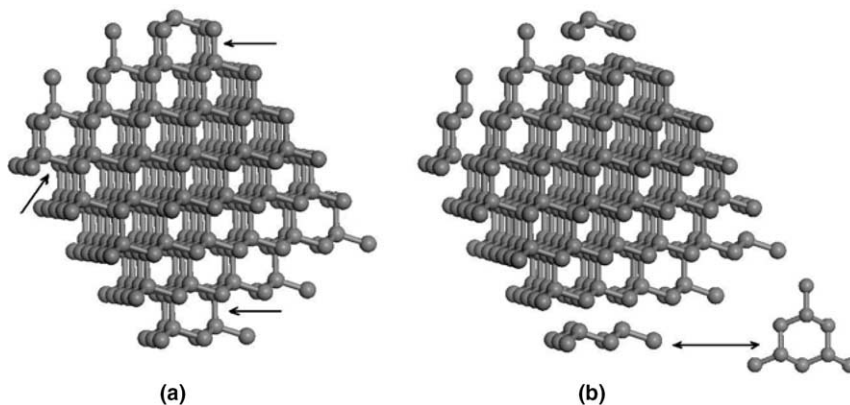


Fig. 7. Formation of graphite fragments by breaking C–C bonds between {111} planes.

diamond surface gradually and the onion-like carbons are similar to the original particles in shape.

4. Conclusion

Diamond nanoparticles graphitize into onion-like carbons by annealing at low temperature. The onion-like carbons begin to form in the range of 1100–1200 °C and the graphitization temperature of diamond nanoparticles changes with the degree of crystallinity corresponding to particle size. All the nanodiamond can transform into onion-like carbons by annealing at 1400 °C for 1 h. The outer shells restrict the inner transformation in a spherical space and thus the interlayer spacing decreases with the increase of graphitic shells number. It is our view that the onion-like carbons inherit the original shape of nanoparticles. The formation process of onion-like carbons includes: formation of graphite fragments, connection and curvature of graphite sheets between diamond {111} planes, and closure of graphite layers.

Acknowledgment

The present research is financially supported by Tianjin Natural Science Foundation: 05YFJZJC01900.

References

- [1] Ugarte D. *Nature* 1992;359:707.
- [2] Oku Takeo, Kuno M, Kitahara H, Narita I. *Int J Inorg Mater* 2001;3:597.
- [3] Johnson MP, Donnet JB, Wang TK, Wang CC, Locke RW, Briinson BE, et al. *Carbon* 2002;40:189.
- [4] Oku T, Narita I, Nishiwaki A. *Diamond Relat Mater* 2004;13:1337.
- [5] Ugarte D. *Carbon* 1995;33:989.
- [6] Qin LC, Iijima Sumio. *Chem Phys Lett* 1996;262:252.
- [7] Kuznetsov VL, Chuvilin AL, Butenko YV, Malkov IY, Titov VM. *Chem Phys Lett* 1994;222:343.
- [8] Kuznetsov VL, Butenko YV, Chuvilin AL, Romanenko AI, Okotrub AV. *Chem Phys Lett* 2001;336:397.
- [9] Okotrub AV, Bulusheva LG, Guselnikov AV, Kuznetsov VL, Butenko YV. *Carbon* 2004;42:1099.
- [10] Gubarevich AV, Kitamura J, Usuba S, Yokoi H, Kakudate Y, Odawara O. *Carbon* 2003;41:2601.
- [11] Hirata A, Igarashi M, Kaito T. *Tribol Int* 2004;37:899.
- [12] Xu NS, Chen J, Deng SZ. *Diamond Relat Mater* 2002;11:249.
- [13] Kuznetsov VL, Chuvilin AL, Moroz EM, Kolomnchuk VN, Shaikhutdinov SK, Butenko YV. *Carbon* 1994;32:873.
- [14] Lee GD, Wang CZ, Yu J, Yoon E, Ho KM. *Phys Rev Lett* 2003;91:265701.
- [15] Kuznetsov VL, Butenko YV, Chuvilin AL, Zaikovskii VI. *Carbon* 2004;42:1057.
- [16] Butenko YV, Kuznetsov VL, Chuvilin AL. *J Appl Phys* 2000;88:4380.
- [17] Tomita Satoshi, Burian A, Dore JC, LeBolloch D, Fujii M, Hayashi S. *Carbon* 2002;40:1469.
- [18] Qian J, Pantea C, Huang J, Zerda TW, Zhao Y. *Carbon* 2004;42:2691.
- [19] Wang CZ, Ho KM, Shirk MD, Molian PA. *Phys Rev Lett* 2000;85:4092.
- [20] Pantea C, Qian J, Voronion GA, Zerda TW. *J Appl Phys* 2002;91:1957.
- [21] Kuznetsov VL, Zilberberg IL, Butenko YV, Chuvilin AL. *J Appl Phys* 1999;86:863.
- [22] Barnard AS, Russo SP, Snook IK. *Diamond Relat Mater* 2003;12:1867.