Diamond & Related Materials xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Reducing dimensions of nanocarbons in electric arc plasma via rapid flow treatment

Bo Li, Yanli Nan, Peng Zhang, Xiaolong Song *

State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:
Received 25 June 2016
Received in revised form 1 September 2016
Accepted 2 September 2016
Available online xxxx

Keywords:
Arc discharge
Nanocarbons
Morphology
Rapid flow

ABSTRACT

The pressure of buffer gas and external fields (e.g. temperature field, magnetic field) significantly influence the non-equilibrium deposition process of nanocarbons in electric arc plasma, resulting in the changes of structure and morphology of arc products. By introducing an external rapid-flow field, the influences of pressures and flow speeds on the dimensions of nanocarbons, including amorphous carbon particles (3-D), graphene sheets (2-D) and carbon nanotubes (CNTs) (1-D), have been investigated under respective conditions. With increased flow speeds, a general trend of reduction in dimension has been observed regardless of the specific type of product. Thus the tubular diameter of CNTs could be controllable by adjusting the flow speed, and, more importantly, single-layer graphene sheets can be readily obtained by introducing high-speed flow under optimized condition of buffer gas. This improvement for arc synthesis may facilitate industrial production of various arc nanocarbons for dimensional requirements. Based on these findings, the possible reasons for the dimensional reduction of arc nanocarbons are discussed on two aspects of material growth and fluid dynamics.

1. Introduction

The discoveries of 0-D fullerenes (C_{60}) in 1985 and 1-D carbon nanotubes (CNTs) in 1990 opened up a new era in science and technology of nanocarbons. In 2004, the breakthrough in preparation of graphene has created an entirely new field for truly 2-D materials. In the past decade, nanocarbons, in particular, CNTs and graphene, as well as their derivatives, have attracted enormous attention due to their excellent physical and chemical properties and ever-growing demand for micro/nanoelectronics, energy storage and conversion, and sensors [1–3].

Since the breakthrough in quantitative synthesis of C_{60} using arc discharge hot plasma between graphite electrodes, direct current (DC) arc discharge technology has attracted more and more attention due to many advantages of such method, including low-cost and high-efficiency preparation, high-quality products, doping-viable synthesis, and huge potential for commercial process. The arc synthesis is usually carried out in a gaseous or liquid environment, creating hot plasma to evaporate the graphite anode. The evaporated carbon radicals (mainly C_1, C_2 and C_3 in arc center, whereas C_4, C_5… in areas distant from the arc zone) coalesce and form nanocarbons depending on the experimental conditions [4]. The temperature of arc center can exceed 4500 K, which thermally anneals the products and removes topological defects during the growth process. To date, DC arc discharge method has been widely used to synthesize high-quality low-dimensional nanocarbons, such as single- and multi-walled CNTs, pure and doped graphene, as well as graphene-based composites [5–8]. In particular, pure and doped graphene sheets can be largely obtained by arc discharge in various conditions (He [9], air [10], H_2 [11], H_2/He [5,12], H_2/N_2/He [13], H_2-inert gas mixtures [14], magnetic field [15], liquid environment [16], different electrode materials such as graphite oxide [11] and SiC [17]). The overall morphology of arc graphene exhibits as a layer of overlapped sheets without any substrate. Most arc graphene reported in the literature have some common structural characteristics as follows: layer number from 10-layer (10L) to bilayer (2L), lateral size ranging from 100 to 300 nm [10–14,18–20]. By adding an external magnetic field, people can acquire relatively larger-area graphene sheets (500–2500 nm), but with thicker layers of 3–15L [15,21]. However, single-layer graphene (SLG) is hard to be found in arc raw soot prepared under normal conditions, indicating the rigorous growth condition of SLG during arc process. Thus the controlled synthesis by adding external condition is probably an effective way to solve this problem. Although the controlled synthesis of nanocarbons using DC arc discharge remains a big challenge and it often suffers from drawbacks such as low purity, the arc nanocarbon materials (e.g. graphene) are demonstrated experimentally to contain low-density topological defects desirable for high-performance micro/nanoelectronics [22].

For controlled synthesis during arc process, one of the most critical problems is dimensional control of the end-products. For example, the diameter and length control of CNTs are basically realized by introducing various catalysts, changing atmosphere conditions or applying magnetic field [7]. In addition, our previous works also demonstrated that the layer number (thickness) of arc graphene can be reduced effectively by rapid flow [5]. In this work, we design a series of experiments to investigate the influences of rapid flow on the dimensional control of common arc carbon products from 3-D to 1-D, that is, amorphous carbon particles (3-D), graphene (2-D) and CNTs (1-D). Our study shows

* Corresponding author.
E-mail address: songxl@mail.xjtu.edu.cn (X. Song).

http://dx.doi.org/10.1016/j.diamond.2016.09.002
0925-9635/

that the dimensions of these nanocarbons can be totally reduced by high-speed flow treatment regardless of their initial dimensions. On the basis of experimental findings, the effect of reducing dimensions of nanocarbons during arc process has been discussed on two aspects of material growth and fluid dynamics.

2. Materials and methods

Briefly, an improved DC arc discharge device with an electric fan centrally facing the arc field was used to prepare arc soot (Fig. 1). Commercial pure graphite (99.99%) rods of 6 and 15 mm in diameters were set as anode and cathode, respectively. The electrodes were installed horizontally in a high-vacuum closed stainless steel chamber filled with buffer gases of He, N_2, and H_2. The direct current was maintained at 80 A and the gap voltage was kept at ~27 V by controlling the distance between two electrodes as a constant of ~2 mm. The discharge time is usually 3–5 min. Raw soot samples were collected from the inner wall of the vacuum chamber. The location of sample collection includes all surfaces of inner wall except the bottom of chamber, because arc slag or ash generated during arc process will deposit onto the surface of furnace bottom. The electric fan speed is controlled by fan voltage and measured using a laser counter with the unit of revolutions per minute (rpm). Owing to technical difficulty to measure the actual flow velocity in arc zone, the fan speed was considered as the indicator of flow speed in discharge zone. Thus small value of fan (flow) speed means weak flow effect introduced by the fan, whereas large value means strong flow effect. The detailed conditions for specific products are listed as follows: 1) Amorphous carbon particles: He atmosphere (20, 50, 80 kPa), flow speeds (0, 2500, 5000, 7500 rpm); N_2 atmosphere (20, 50 kPa), flow speeds (0, 7500 rpm). 2) Arc graphene: H_2 atmosphere (40, 80 kPa), flow speeds (0, 2500, 5000, 7500, 11,500 rpm); He/H_2 mixtures (vol ratio 10:1, total pressures 20, 40, 60, 80 kPa; and vol ratio 1:1, total pressures 20, 40, 60, 80 kPa), flow speeds (0, 2500, 5000, 7500, 11,500 rpm). 3) CNTs: He/N_2 mixtures (vol ratio 1.5:1, total pressure 40 kPa), carbon and catalyst powders (C:Ni:Co = 95:3:2, wt%), flow speeds (0, 800, 2500, 5000, 7500 rpm).

The two-step separation procedures were carried out by an ultrasonic instrument (DR-MH20, Derui) and a high-speed centrifuge (TGL-16). The solvent contains a mixture of ethanol and deionized water in a volume ratio of 1:4. A solution of graphene with a concentration of 0.25 mg × mL^{-1} is processed by 2 h sonication and 30 min centrifugation with speed of 12,000 rpm. Then the upper part of the solution (supernatant) was transferred for the following measurements. With centrifugal speed of 12,000 rpm, the dispersion of graphene sheets can achieve a very high level to provide a large number of individual graphene sheets with varying layers.

The bright-field imaging of the samples were acquired by employing a transmission electron microscope (TEM, JEOL-200CX) and a high-resolution transmission electron microscope (HRTEM, JEM-2010F). The acceleration voltages of TEM and HRTEM are 120 and 200 kV, respectively. The size of the selected-area aperture is ~200 nm in our experiment.

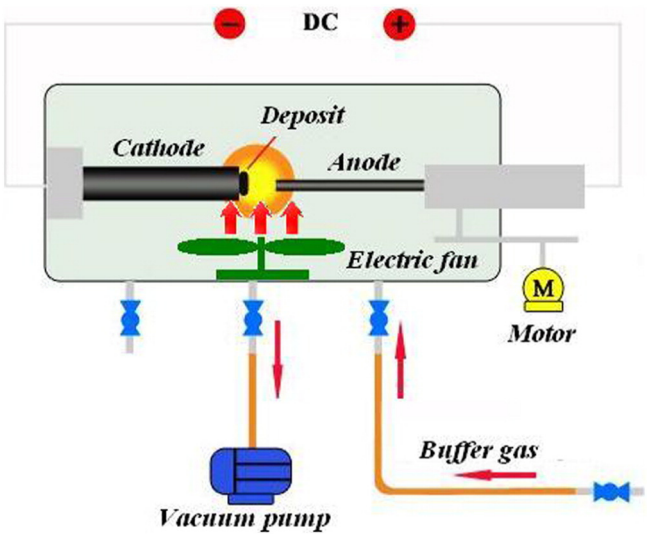

Fig. 1. Schematic of an improved DC arc device with the introduction of an electric fan.

3. Results and discussion

3.1. Amorphous carbon

Amorphous carbon is the most common kind of arc carbon products under most reactive conditions. In this section, the influences of pressures of He and N_2 buffer gases and the flow speed on the dimensions of amorphous carbon particles have been investigated. In He atmosphere, the arc soot containing nearly 100% amorphous carbon have been readily achieved under the experimental conditions. Fig. 2 exhibits the morphology of amorphous carbon obtained under different conditions of He pressures and flow speeds. In 80 kPa He atmosphere, the morphological differences between samples under flow speeds of 0 and 7500 rpm are shown in Fig. 2(a) and (b), respectively. One can see that the mean size of amorphous carbon under 7500 rpm decreases largely compared with the counterpart untreated by flow. In Fig. 2(c) and (d), the flow-induced dimensional reduction of amorphous carbon is also shown in 20 kPa He atmosphere. Moreover, without the flow effect, the mean size of amorphous carbon produced under low pressure is smaller than that of samples produced under high pressure, indicating that the dimension of amorphous carbon can be either decreased by the pressure reduction of buffer gas or the introduction of high-speed flow. In all experimental conditions, the general trend of dimensional changes of amorphous carbon can be concluded in Fig. 2(e). Obviously, the dimension of amorphous carbon produced in high pressure is more affected by rapid flow than those produced in low pressure.

In N_2 atmosphere, all soot samples are basically amorphous carbon particles under four discharge conditions. TEM observation exhibit the same trend of dimension changes of amorphous carbon in contrast to those produced in He atmosphere. The mean diameters of these particles change from 40 to 20 nm in 20 kPa N_2 atmosphere with flow speeds from 0 to 7500 rpm. In 50 kPa N_2 atmosphere, the mean diameters change from 50 to 30 nm.

3.2. Arc graphene

When graphite anode evaporated in H_2 atmosphere, the consumption rate of the anode is much faster than in other gases, showing that the fast reaction between carbon and hydrogen atoms (ions), as well as the generation of hydrocarbon gases. The generation of hydrocarbon gases can be probed by the rise of chamber pressure, as well as less samples collected from the inner wall. Fig. 3(a) and (b) exhibits the different morphology of arc graphene under conditions of 40 kPa, 0 rpm and 80 kPa, 7500 rpm, respectively. Without the flow effect, the morphology of graphene looks alike according to TEM observation, exhibiting as an overlapping view which graphene sheets tangled with each other. When introducing high-speed flow, e.g. 7500 rpm, the graphene sheets seems more dispersible and thinner. As for the lateral size, rapid flow has no obvious effect on the size changes.

In He/H_2 mixtures, the main products basically consist of amorphous carbon and graphene sheets. When evaporating graphite in He/H_2 mixtures, the growth of amorphous carbon and graphene are competitive with respect to the partial pressure of hydrogen. TEM observations exhibit that high pressure of hydrogen facilitates the formation of graphene sheets, while high pressure of helium leads to the curvature of flat graphene planes and increased production of amorphous carbon

Please cite this article as: B. Li, et al., Reducing dimensions of nanocarbons in electric arc plasma via rapid flow treatment, Diamond Relat. Mater. (2016), http://dx.doi.org/10.1016/j.diamond.2016.09.002