A method and a device for production of fullerene-related carbon nanotubes and fullerenes in direct current arc discharge between two graphite electrodes are disclosed. Two features distinctive from conventional arc discharge technique providing remarkably high productivity of the present method are introduced. The first feature comprises means for maintaining an optimal temperature of anode end surface to suppress formation of large carbon clusters and microcrystalline carbon particles useless for synthesis of carbon nanotubes and fullerenes. The second one comprises means for maintaining an optimal concentration of carbon and catalyst vapor in vapor generation zone to ensure optimal yields of carbon nanotubes and fullerenes. Airtight plug-in cartridges are used to supply consumable electrodes and catalyst material inside closed-loop device without process being stopped. The means to perform automatic continuous feeding of consumable electrodes and catalyst, pneumatic transportation of condensables and their automatic continuous discharge are also described.
CONTINUOUS PRODUCTION OF CARBON NANOTUBES AND FULLERENES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

REFERENCE TO SEQUENCE LISTING, A TABLE, OR A COMPUTER PROGRAM LISTING COMPACT DISK APPENDIX

[0003] Not Applicable

BACKGROUND OF THE INVENTION

[0004] The present invention relates to such nanostructures as carbon nanotubes and fullerences and a continuous method of their production. Fullerene C,nanotube and higher fullerences were first produced in gram quantities in an arc discharge between two graphite electrodes in 1990 [W. Kretschmer et al. "Solid C60: A new form of carbon", Nature, 347, 354-357 (1990)]. It is still the major technique in commercial production of fullerences, which is thought characterized by limited productivity.

[0005] Carbon nanotubes are a tubular form of carbon closely related to the C,nanotube molecule, which can be also produced by the mentioned above arc discharge technique with addition of metal catalyst. Carbon nanotubes produced in an arc discharge are called fullerene-related nanotubes. They have much less structure defects and possess superior properties in comparison with nanotubes produced by alternative methods like, for example, carbon vapor deposition (CVD) method. Carbon nanotubes production by arc discharge technique possesses the same disadvantages as fullerene production—limited productivity and high final product cost. Numerous optimization efforts have demonstrated that reasonable yields of said carbon nanostructures can be produced by arc discharge technique in a very narrow area of process parameters comprising usage of graphite electrodes 4-10 mm in diameter, electric current 50-100 A and reactor pressure 30-200 Torr [Bogdanov A. A., Deininger, D., Dyuzheev, G. A. Development Prospects of the Commercial Production of Fullerences, Zhurnal Tekhnicheskoi Fiziki, 45(5), 521-527 (2000)]. At the same time productivity of a single arc could not exceed the limit of a few grams of carbon nanotubes or fullerences per hour.

[0006] We believe there are two major reasons accounting for the mentioned productivity limitation of arc discharge technique. The first one represents the fact that carbon vapor concentration in vapor generation zone is a function of anode evaporation rate. Formation of carbon nanotubes and fullerences is a polyatomic process, which is quite sensitive to concentration of reaction components. That means that nanotube and fullerence yields are also functions of anode evaporation rate and productivity of existing arc discharge technique can’t be scaled up in principle because any attempt to increase evaporation rate would increase carbon vapor concentration and promote primary formation of carbon black particles, which will dramatically reduce yield of the desired nanostructures. In order to scale up productivity of arc discharge technique it is necessary to make anode evaporation rate and carbon vapor concentration mutually independent.


[0008] A method of the present invention eliminates both mentioned above negative phenomena and enables remarkably high productivity and reasonable yields of both fullerene-related nanotubes and fullerences produced by arc discharge technique. Since the method is easily scalable only economical considerations of the most appropriate scale and the largest size of graphite electrodes readily available could limit its utmost productivity.

[0009] Commercially suitable process necessarily requires continuous type of production. There are a number of publications where authors disclose one or several aspects of continuous fullerene production. Thus, in the work [Smalley R. E., Haehler R. E. Electric arc process for making fullerences. U.S. Pat. No. 5,227,038; 1993] authors described a closed-loop device for fullerene generation comprising means for filtration of condensables. The work [Lorents D. C., Malhotra R. Process and apparatus for producing and separating fullerences. U.S. Pat. No. 5,304,366; 1994] also presents a closed-loop reactor for fullerene synthesis comprising means to separate different types of fullerences in temperature gradient. The work [Duzhev G. A., Basargin I. V., Filippov B. M., Aleskseev N. I., Afanasiev D. V., Bogdanov A. A. Method for producing fullerene-containing carbon and device for carrying out said method. WO 02/096800, 2002] introduced inert gas circulating system and considered continuous movement of graphite electrode inside the electric arc zone. Since carbon nanotubes are less mature then fullerences we were not able to find out any explicit descriptions of their continuous production by arc discharge technique.

[0010] Present invention bridges this gap and introduces detailed description of a closed-loop device for continuous production of carbon nanotubes and fullerences comprising continuous automated feeding of graphite electrodes and catalyst into vapor generation zone, usage of airtight interchangeable plug-in cartridges providing uninterruptible source of fresh carbon and catalyst, pneumatic transportation of condensables and their automated discharge outside of said closed-loop device.
BRIEF SUMMARY OF THE INVENTION

This invention provides a method and a device for continuous production of fullerene-related carbon nanotubes and fullerenes in arc discharge between two graphite electrodes, one of which is a movable consumable anode and another one is a motionless non-consumable cathode. Vapor generation zone is maintained between said graphite electrodes. Catalyst in a form of metal wire or fine metal powder is fed into vapor generation zone through perforation in cathode body. Since the invention presents continuously working closed-loop device uninterruptible supply of fresh portions of catalyst is provided by means of interchangeable airtight plug-in cartridges. Consumable graphite electrodes are also delivered inside the closed-loop device by means of mechanisms for electrode automatic jointing. Jointed graphite electrodes are continuously fed into vapor generation zone by conveyor transportsers equipped with spring clamps. Injertion for our and airtight plug-in parallel to anode end surface maintains its optimal temperature and suppresses formation of large carbon clusters and micro-crystallite carbon particles in vapor generation zone. Noble gas flow coaxial to graphite electrodes maintains an optimal concentration of carbon vapor in vapor generation zone to ensure optimal yields of carbon nanotubes and fullerenes. Condensables containing fullerene-related carbon nanotubes and fullerenes are pneumatically transported by a noble gas flow outside of vapor generation zone, cooled down, filtered, collected in a storage bin and automatically discharged out of closed-loop device. Carbon nanotubes and fullerenes are recovered from discharged condensables. These and other features of the invention will become clear from the following detailed description.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is a schematic illustration of the device for continuous production of fullerene-related carbon nanotubes and fullerenes according to the invention.

FIG. 2 is a detailed illustration of the arc discharge section comprising several means to direct a noble gas flow into vapor generation zone.

FIG. 3 is a detailed illustration of anode feeding section comprising conveyor transporter equipped with spring clamps and airtight plug-in cartridge containing multiple graphite electrodes.

FIGS. 4A and 4B are detailed illustrations of catalyst feeding section for catalyst in a form of a metal wire or a fine metal powder correspondingly comprising automatic feeder and airtight plug-in cartridge containing fresh portion of catalyst. FIGS. 4A, View A and View B-B demonstrate the means for preventing catalyst material melting inside cathode body perforation while feeding into vapor generation zone.

DETAILED DESCRIPTION OF THE INVENTION

A method and a device for continuous production of fullerene-related carbon nanotubes and fullerenes are disclosed. FIG. 1 represents a closed-loop device, which constitutes an airtight water-cooled chamber 1, heat exchanger 2, filter 3, storage bin 4 with automatic discharge valve 21 and re-circulation pump 5. Chamber 1 comprises three interconnected sections—an arc discharge section 6 with vapor generation zone 7 situated between anode 8 and cathode 9 possessing perforation 22, anode feeding section 10 with anode feeding mechanism 11 and airtight plug-in cartridge 12 containing multiple graphite electrodes 13 and catalyst feeding section 14 with catalyst feeding mechanism 15 and airtight plug-in cartridge 16 containing catalyst 17 in a form of a metal wire or a fine metal powder. Heat exchanger 2 comprises water-cooled jacket 18 and screw conveyor 19 with drive 20. Aircar section 6 shown in FIG. 2 comprises vapor generation zone 7 between anode 8 and cathode 9, cathode holder 23, gas distributor 26, gas nozzles 27 and 28 and gas outlet 24. Jet flows 29 and 30 and distributed flow 31 of a noble gas are created inside the arc discharge section 6. Anode feeding section 10 shown in FIG. 3 comprises two conveyor transporters 32 equipped with multiple spring clamps 33, guiding slide rails 34 and pulleys 35. Airtight plug-in cartridge 12 with multiple graphite electrodes 13 is equipped with pushing mechanism 36 and revolving mechanism 37 possessing a flexible head 38 supported by compression spring 39. Graphite electrodes 8 and 13 have female threads 40 on both ends. Graphite nipples 41 with two male threads joint them as is customary in metallurgy industry. Catalyst feeding section 14 for catalyst in a form of a metal wire is shown in FIG. 4A. It comprises an airtight plug-in cartridge 16 containing a coil of catalyst wire 17, wire feeder 15 and aligning rollers 42. Referring to FIGS. 4A, View A and View B-B cathode 9 has central perforation 22 ending in widening 44 and several side perforations 45 ending in widening 44 as well to create gas shield 46. Catalyst feeding section 14 for catalyst in a form of a fine metal powder is shown in FIG. 4B. It comprises an airtight plug-in cartridge 16 containing a portion of a fresh catalyst powder 17, catalyst feeding mechanism 15 comprising dispenser 47 and mixer 48.

Referring to FIG. 1 a method of the present invention comprises establishing a vapor generation zone 7 in an atmosphere of a noble gas within an arc discharge section 6 by starting and maintaining direct current (DC) arc discharge between two graphite electrodes 8 and 9. One of the electrodes is a movable consumable anode 8, while another one is a motionless non-consumable cathode 9. Carbon vapor for production of desired carbon nanostructures is generated by means of movable anode 8 evaporation. Graphite electrodes 13 supplied within interchangeable airtight plug-in cartridge 12 are automatically jointed with anode 8 and continuously fed into vapor generation zone 7 by conveyor transporter 11 located in the section 10 of the chamber 1. At the same time catalyst 17 supplied within interchangeable airtight plug-in cartridge 16 is fed into vapor generation zone 7 by feeding mechanism 15 located in the section 14 through perforation 22 in cathode body 9. Catalyst 17 can represent a coil of metal wire or a portion of fine metal powder, which defines the specific design of feeding mechanism 15. Arc discharge section 6 contains means to maintain an optimal temperature of anode 8 surface and an optimal concentration of carbon and catalyst vapor in vapor generation zone 7 by injection of a noble gas. Optimally diluted carbon and catalyst vapor cool down and form condensables containing fullerene-related carbon nanotubes and fullerenes. The condensables are pneumatically transported from arc discharge section 6 to heat...
exchanger 2, where they experience further cooling. Condensables deposited on the inner walls of heat exchanger 2 are cleaned by screw conveyor 19 and moved to storage bin 4. The rest of condensables is deposited on filter 3, which is cleaned by periodic pulses of reversed gas flow, vibrations or any other effective means to clean filter. Both condensables from heat exchanger 2 and filter 3 are collected at the same storage bin 4 to simplify their automatic discharge procedure. Condensables discharged through automatic discharge valve 21 are subjected to recovery of carbon nanotubes and fullerenes. Re-circulation of a noble gas flow is accomplished by oil-less gas pump 5. Re-circulating noble gas is separated into three flows supplied to arc discharge section 6, anode feeding section 10 and catalyst feeding section 13. Noble gas flow supplied to anode feeding section 10 provides there slight overpressure, which prevents penetration of condensables and protects conveyor mechanism 11 from clogging up.

[0018] Functioning of arc discharge section 6 is more specifically demonstrated in FIG. 2. Jet flow 29 of a noble gas parallel to anode end surface is injected through a gas nozzle 28 to maintain optimal temperature of anode end surface. Jet flow 29 provides effective removal of carbon clusters just evaporated from the anode end surface and facilitates effective evaporation of new carbon clusters. Since evaporated clusters take away excessive energy they cool down anode surface suppressing formation of large carbon clusters and micro-crystallite carbon particles in vapor generation zone 7. The amount and speed of jet flow 29 allows controlling anode surface temperature without sacrificing much of anode evaporation rate. A noble gas injected through gas nozzle 27 creates jet flow 30, which is a counter-flow to the jet flow 29. Jet flow 30 prevents excessive deposition of condensables on the inner walls of section 6. An additional noble gas flow 31 is supplied through gas distributor 26 in axial direction from cathode to anode to provide an optimal concentration of carbon and catalyst vapor mixture and transport resulting gas flow directly towards gas outlet 24. Optimal ratio between gas flows 29, 30 and 31 ensures high productivity and high yield of a method.

[0019] Referring to FIG. 3 the detailed procedure of anode feeding comprises the following steps. Anode 8 with female threads 40 on both ends is initially installed between spring clamps 33 of two conveyor transporters 32 and the bottom edge of anode 8 coincides with the bottom edge of the section 10. Pushing mechanism 36 installed in the plug-in cartridge 12 moves the package of electrodes 13 and positions the leftmost electrode coaxial with anode 8. The head 38 of revolving mechanism 37 fixes itself at the bottom of electrode 13 by friction forces, moves electrode 13 up and joints electrodes 8 and 13 together by rotation of electrode 13. The compression spring 39 ensures necessary pressing of electrode 13 towards electrode 8 while jointing. Conveyor pulleys 35 rotate as shown in FIG. 3, spring clamps 33 embrace movable anode 8 and gradually transport it towards vapor generation zone 7. Positive electric contacts are attached to the stationary axes of conveyor pulleys 35 and electric current is supplied through spring clamps 33 to movable anode 8. When the bottom edge of electrode 13 coincides with the bottom edge of the section 10 new graphite electrode is supplied from plug-in cartridge 12, jointed with the current anode and the described above procedure repeats itself until all electrodes 13 are fed. Then the plug-in cartridge 12 is quickly reinstalled without process being stopped.

[0020] Catalyst suitable for synthesis of carbon nanotubes mainly comprises transition metals from the forth and the fifth periods of the periodic system of elements, preferably Fe, Co, Ni and Y or their alloys. Referring to FIG. 4A if said catalyst is available in a form of a metal wire its automated feeding is performed in the following way. A coil of catalyst wire 17 is supplied from airtight interchangeable plug-in cartridge 16, straightened by aligning rollers 42 and gradually transported by feeding mechanism 15 through perforation 22 in cathode body 9 into vapor generation zone 7. Cathode 9 temperature gradually rises towards its end and may noticeably exceed melting point of catalyst material. Therefore, some precautions have to be taken to prevent melting of catalyst inside the cathode body. Widening 44 at the end of cathode body shown in FIG. 4A, View A prevents direct contact of the walls of cathode body perforation 22 with catalyst 17 in the area of possible catalyst melting. To prevent catalyst vapor deposition on inner sidewalls of the widening 44 gas shield 46 is created by injection of a noble gas through side perforations 45 in cathode body. The arrangement of side perforations 45 is shown in FIG. 4A, View B-B. If catalyst is available in a form of a fine metal powder its automated feeding is performed as shown in FIG. 4B. A fresh portion of powder catalyst 17 is supplied from airtight interchangeable plug-in cartridge 16, dressed in dispenser 47, mixed with a noble gas flow in mixer 48 and pneumatically transported through perforation 22 in cathode body 9 into vapor generation zone 7. The same precautions as in the case of metal wire catalyst are taken to prevent melting of fine metal powder inside the cathode body.

That which is claimed is:

1. A method for continuous production of carbon nanotubes and fullerenes comprising:

a. establishing vapor generation zone in an atmosphere of a noble gas by starting and maintaining direct current arc discharge between two graphite electrodes, one of which is a movable consumable anode and another one is a motionless non-consumable cathode;

b. providing means for maintaining an optimal temperature of anode end surface to suppress formation of large carbon clusters and micro-crystallite carbon particles in vapor generation zone;

c. providing means for maintaining an optimal concentration of carbon and catalyst vapor in vapor generation zone to ensure optimal yields of carbon nanotubes and fullerenes;

b. providing means for maintaining an optimal temperature of anode end surface to suppress formation of large carbon clusters and micro-crystallite carbon particles in vapor generation zone;

d. continuous automated feeding of a movable anode into vapor generation zone;

e. continuous automated feeding of a catalyst for carbon nanotube synthesis in a form of a metal wire or a fine metal powder into vapor generation zone through central perforation in cathode body;

f. formation of condensables outside of vapor generation zone containing fullerene-related carbon nanotubes and fullerenes;
g. pneumatic transportation of condensables by a noble gas flow, their cooling, filtration and collection in a storage bin and a noble gas flow re-circulation;

h. automated discharge of condensables from the storage bin and recovery of carbon nanotubes and fullerenes.

2. The method as set forth in claim 1 wherein the means for maintaining optimal temperature of anode end surface comprise jet flow of a noble gas parallel to anode end surface providing effective removal of just evaporated carbon clusters and facilitating effective evaporation of new clusters.

3. The method as set forth in claim 1 wherein the means for maintaining an optimal concentration of carbon and catalyst vapor in vapor generation zone comprise an admixture of carbon vapor with a noble gas flow coaxial with electrodes and directed from cathode to anode.

4. The method as set forth in claim 1 wherein the means for maintaining an optimal concentration of carbon vapor in vapor generation zone also serve for pneumatic transportation of condensables.

5. The method as set forth in claim 1 wherein precautions are taken to prevent melting of catalyst material inside the cathode body while catalyst is fed into vapor generation zone through perforation in cathode body.

6. A device for continuous production of carbon nanotubes and fullerenes, which represents closed-loop system and includes:
   a. an airtight water-cooled chamber comprising an arc discharge section containing vapor generation zone between two graphite electrodes, an anode feeding section containing means to provide automated jointing of separate graphite electrodes and their gradual transportation into vapor generation zone and a catalyst feeding section containing means to provide continuous supply of catalyst through central perforation in cathode body into vapor generation zone;
   b. an interchangeable airtight plug-in cartridge containing multiple graphite electrodes for non-stop device operation;
   c. an interchangeable airtight plug-in cartridge containing catalyst in a form of metal wire or a fine metal powder for non-stop device operation;
   d. means for maintaining an optimal temperature of anode surface and an optimal concentration of carbon vapor in vapor generation zone comprising at least one gas nozzle and at least one gas distributor placed within arc discharge section of the airtight chamber;
   e. means for pneumatic transporting of the condensables and noble gas flow re-circulation;
   f. a heat-exchanger to maintain constant temperature of the re-circulating noble gas flow comprising means for continuous cleaning heat exchanger inner walls from the condensables;
   g. a filter to separate the condensables from a noble gas flow comprising means for filter automatic self-cleaning;
   h. a storage bin for filtered condensables comprising means for automated discharge of said condensables outside of a storage bin.

7. The device as set forth in claim 6 wherein automated jointing of separate graphite electrodes is accomplished by at least two mechanisms installed in plug-in cartridge—pushing mechanism providing coaxial position of two electrodes and revolving mechanism jointing said electrodes by the means of female threads on both electrode ends and jointing nipple.

8. The device as set forth in claim 6 wherein gradual transportation of graphite electrodes into vapor generation zone is accomplished by two conveyor transporters equipped with spring clamps tightly embracing said electrodes from the two opposite sides.

9. The device as set forth in claim 6 wherein the means for graphite electrodes gradual transportation into vapor generation zone are used to supply electric current to said electrodes.

10. The device as set forth in claim 6 wherein said catalyst for carbon nanotubes synthesis is supplied in a form of a metal wire or a fine metal powder and the means for its continuous supply into vapor generation zone are presented by any standard or customized wire or powder feeder suitable for the purposes of the present invention.

11. The device as set forth in claim 6 wherein said cathode body has a central perforation for a catalyst feeding ending in a widening and several side perforations ending in the same widening to create protective gas shield and prevent catalyst vapor deposition on the inner sidewalls of the widening.

12. The device as set forth in claim 6 wherein maintaining an optimal temperature of anode end surface comprises two gas nozzles creating two jet counter-flows with their collision point located outside of vapor generation zone.

13. The device as set forth in claim 6 wherein recirculation of a noble gas flow is accomplished by oil-less gas pump, oil-less gas compressor or other similar means.

14. The device as set forth in claim 6 wherein recirculating noble gas is separated into at least three flows supplied to arc discharge section, anode feeding section and catalyst feeding section of the airtight chamber.

15. The device as set forth in claim 6 wherein screw conveyor accomplishes continuous cleaning of condensables from the heat exchanger inner walls.

16. The device as set forth in claim 6 wherein deposited on filter surface condensables are cleaned by periodic pulses of reversed gas flow, vibration or any other effective means for filter cleaning.

17. The device as set forth in claim 6 wherein condensables from filter and heat exchanger are collected at the same storage bin to simplify procedure of their discharge.