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(54) **BORON NITRIDE NANOTUBE FIBRILS AND YARNS**

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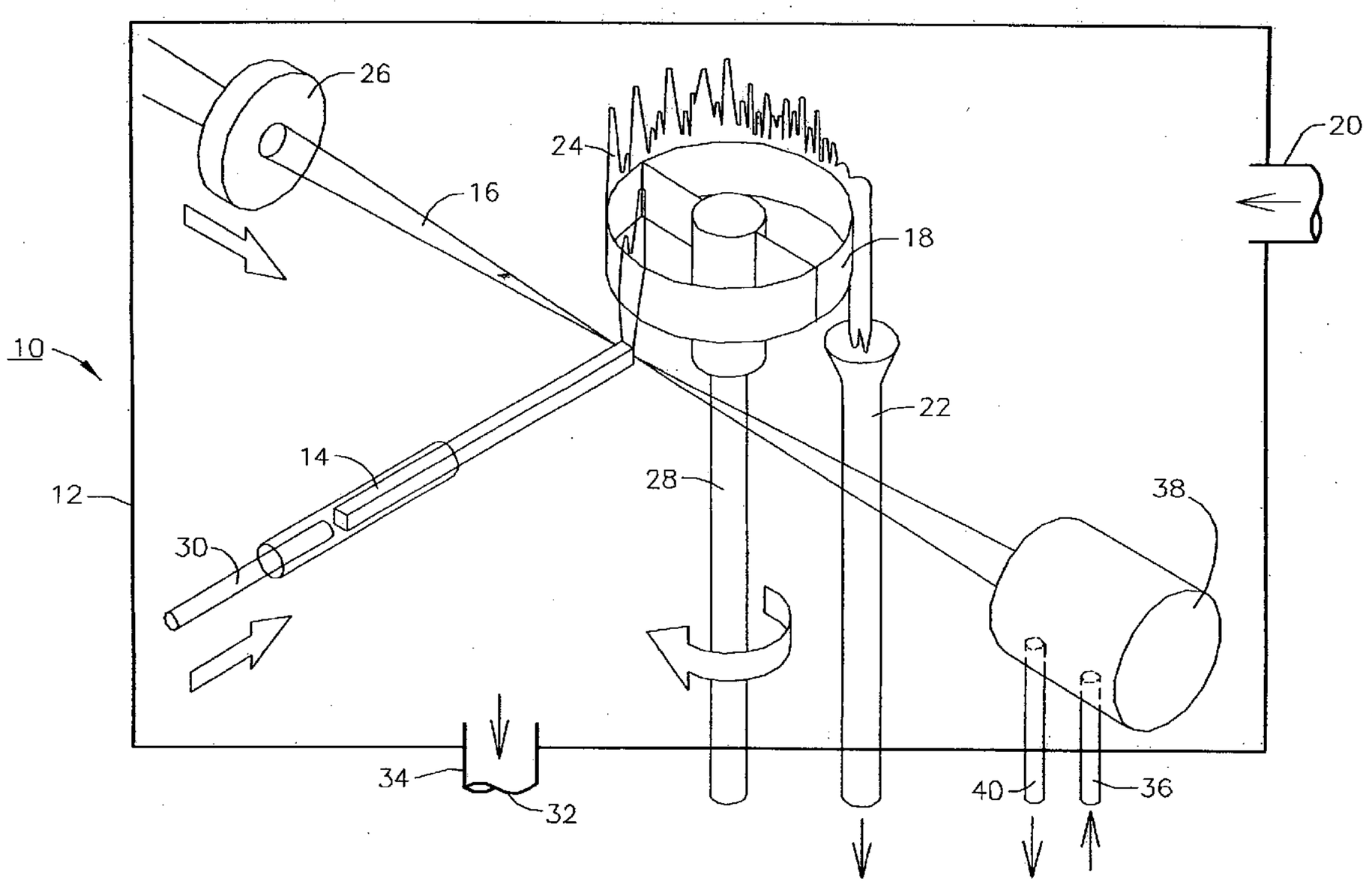
(57) **ABSTRACT**

A method for the production of long, high aspect ratio boron nitride nanotubes and boron nitride nanotube fibrils composed of single or few walled boron nitride nanotubes aligned in bundles of nanotubes 20 μm and longer at a rate of above about 1 meter per second. Nanotube yarns comprised of twisted bundles of such nanotube fibrils are also described.



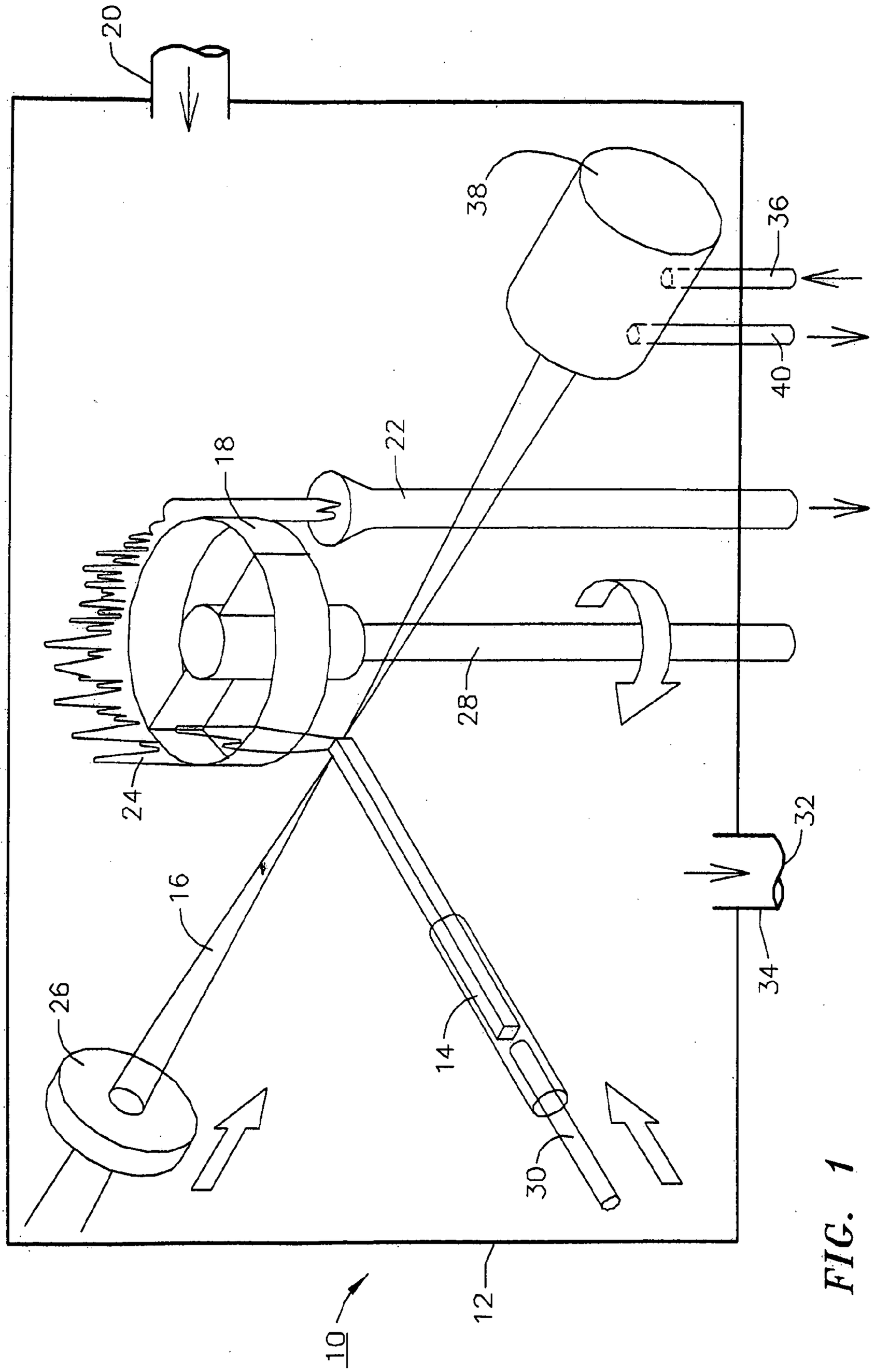


FIG. 1

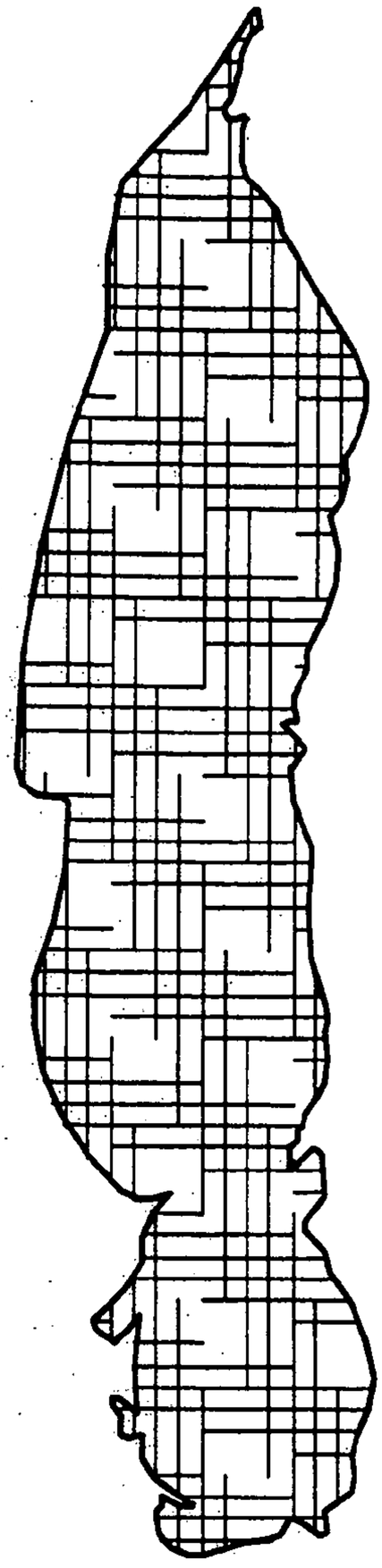


FIG. 2

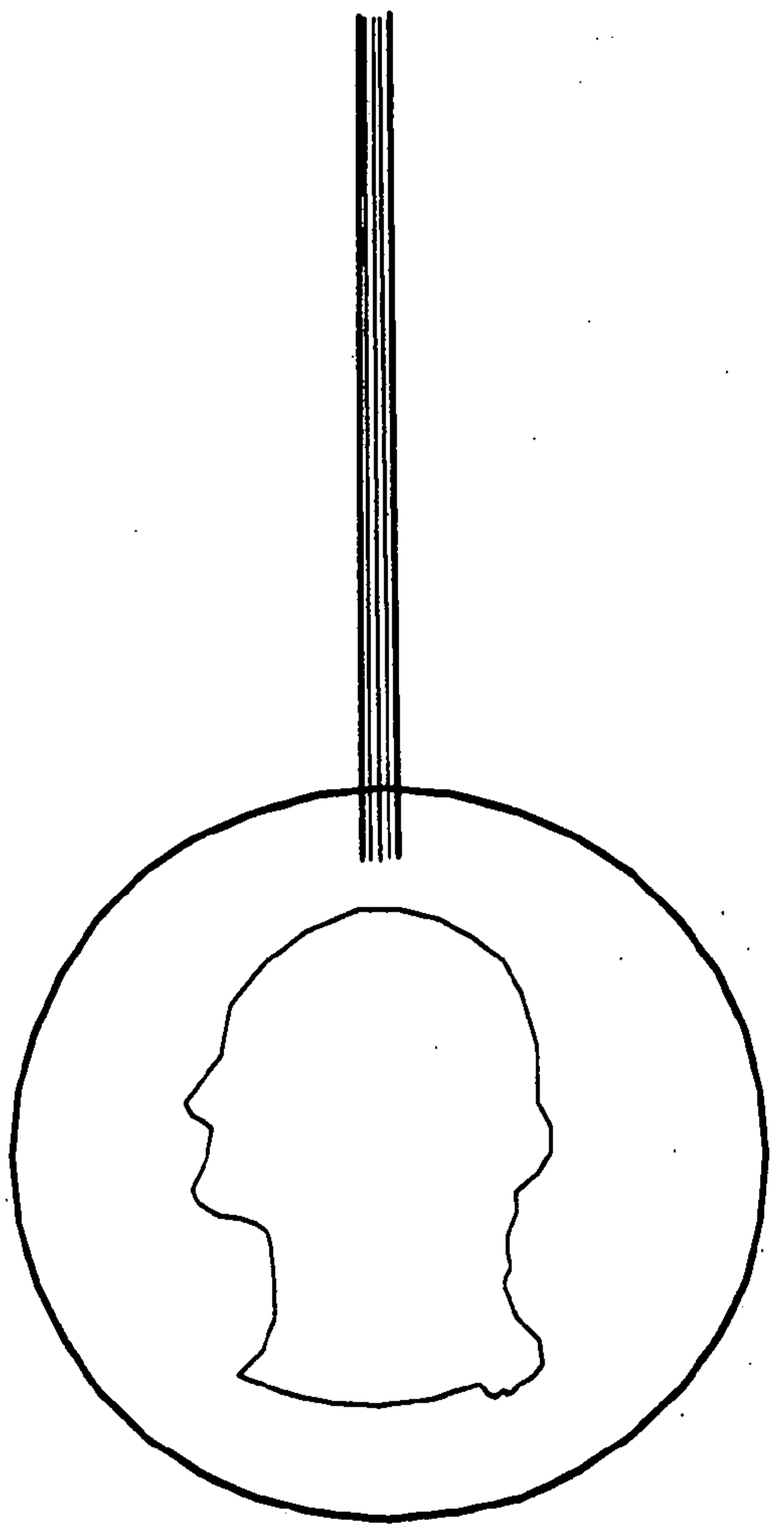


FIG. 3

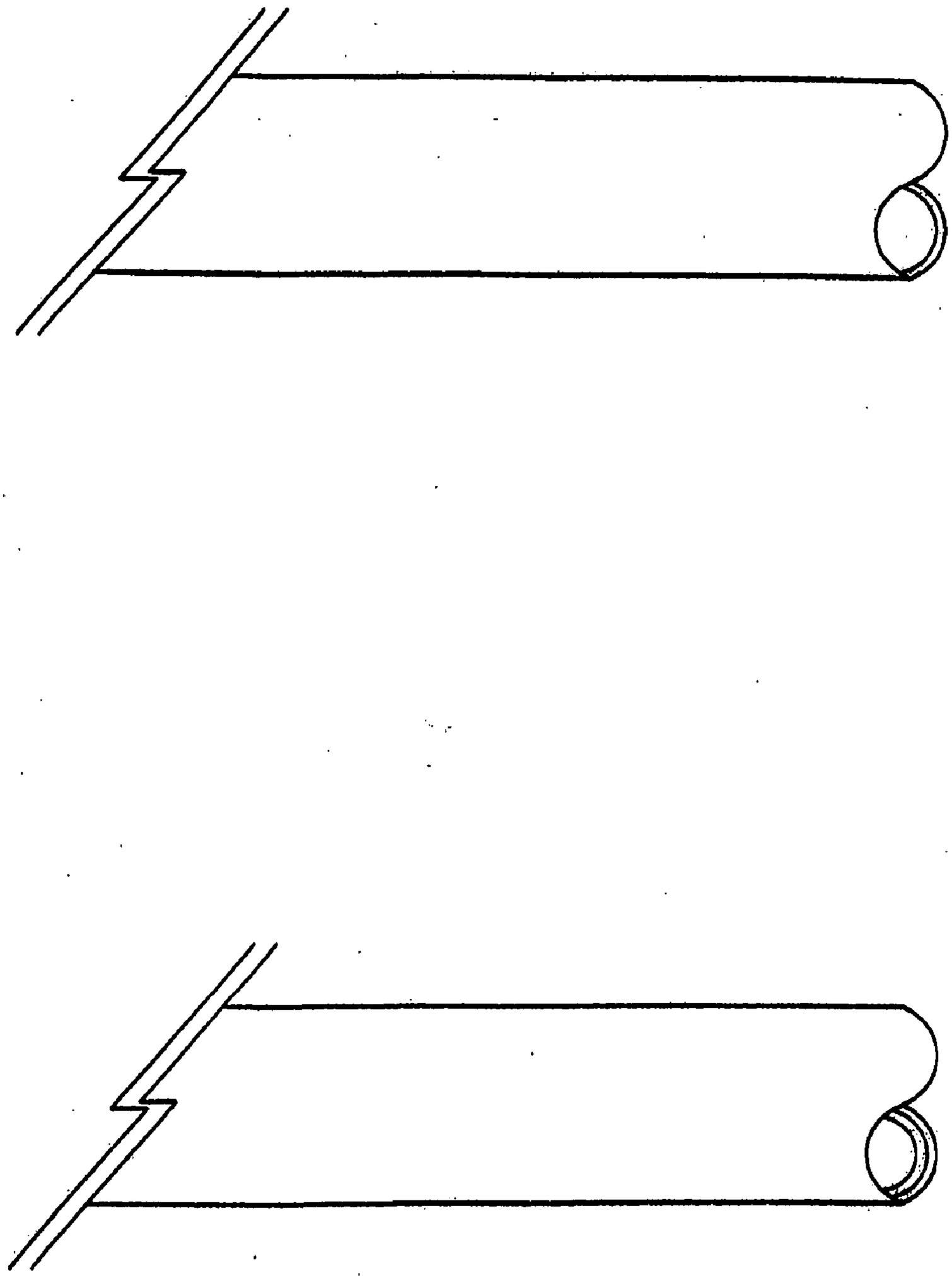


FIG. 4

BORON NITRIDE NANOTUBE FIBRILS AND YARNS

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 12/322,591 filed Feb. 4, 2009 for "Apparatus for the Production of Boron Nitride Nanotubes".

[0002] The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Cooperative Agreement No. NCC-1-02043 awarded by the National Aeronautics and Space Administration and Management and Operating Contract DE-AC05-060R23177 from the United States Department of Energy.

FIELD OF THE INVENTION

[0003] The present invention relates to the production of nanostructures and more particularly to a method for the high rate production of long stranded boron nitride nanotube fibers, boron nitride nanotube fibrils and boron nitride nanotube yarns.

BACKGROUND OF THE INVENTION

[0004] Since the announcement of the successful synthesis of relatively high-aspect-ratio few-walled boron nitride nanotubes (FW-BNNTs) in 1995, little progress has been made in the scale-up of their synthesis. As a demonstration, in spite of the theoretical capabilities of FW-BNNTs to provide high strength-to-weight, high temperature resistance, piezo-electric actuation, and radiation shielding (via the boron content), the aerospace industry still relies on micron-sized graphite or boron fibers for structural applications. FW-BNNTs are not widely used in aerospace and other manufacturing industries generally most willing to pay a premium for high performance, because of the microscale of such materials that are currently available.

[0005] To date, relatively high-aspect ratio FW-BNNTs have been produced in small amounts (from individual tubes to milligrams) by arc-discharge or laser heating methods. A separate class of boron nitride nanotubes has also been produced by chemical vapor deposition of nitrogen compounds (e.g. ammonia) over ball-milled precursors, but these tubes are of larger diameter and do not exhibit the continuous crystalline sp2-type bonding structure which has drawn most theoretical interest.

[0006] Boron nitride nanotubes (BNNTs) are desired for their exceptional mechanical, electronic, thermal, structural, textural, optical, and quantum properties. Most of these applications require long BNNTs to impart these desirable properties over macroscopic distances in real-world objects and devices. Although progress has been made in synthesizing long strands and yarns of carbon nanotubes, similar progress has not been reported for BNNTs.

[0007] International Publication Number WO 2009/017526 published Feb. 5, 2009 describes a process for the production of at least centimeter-long boron nitride nanotubes. The disclosure of this application is hereby incorporated herein by reference in its entirety.

[0008] U.S. patent application Ser. No. 12/322,591 filed Feb. 4, 2009 describes an apparatus for the large scale production of boron nitride nanotubes comprising; a pressure chamber containing; a continuously fed boron containing target; a source of thermal energy preferably a focused laser beam; a cooled condenser; a source of pressurized nitrogen gas; and a mechanism for extracting boron nitride nanotubes that are condensed on or in the area of the cooled condenser from the pressure chamber. The disclosure of this application is similarly hereby incorporated herein by reference in its entirety.

[0009] While each of the foregoing Applications describe highly useful and efficient methods and apparatus for the production of BNNTs, they have not demonstrated the production of boron nitride fibrils that can be bunched and spun into yarn. Accordingly, there remains a need for methods of producing BNNTs that exhibit much larger aspect ratios (i.e. are much longer) that can be processed into useful macroscale yarns.

OBJECTS OF THE INVENTION

[0010] It is therefore an object of the present invention to provide a method for the production of boron nitride nanotube fibrils that can be relatively easily spun or otherwise processed into boron nitride nanotube yarns.

[0011] It is another object of the present invention to provide a method for the production of such large aspect ratio BNNT fibril at rates in excess of one meter per second.

SUMMARY OF THE INVENTION

[0012] According to the present invention there is provided a method for the production of very high aspect ratio boron nitride nanotubes and fibrils composed of single or multi-walled nanotubes aligned in bundles of tubes 20 μm and longer at a rate of above about 1 meter per second. nanotube yarns comprised of twisted bundles of such nanotube fibrils are also described.

DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1** is a schematic side view of the apparatus described in U.S. patent application Ser. No. 12/322,591 and useful in the successful practice of the present invention.

[0014] FIG. **2** shows a collected mass of boron nitride nanotube fibrils harvested in accordance with the present invention.

[0015] FIG. **3** shows a yarn formed by simply spinning the boron nitride fibril mass shown in FIG. **2**.

[0016] FIG. **4** is a schematic representation of transmission electron microscope views of single and three-walled nanotubes in accordance with the present invention.

DETAILED DESCRIPTION

[0017] The benefits of the present invention are achieved by providing a process for producing boron nitride nanotubes and nanostructures, which comprises:

[0018] (a) providing a boron-containing target in a chamber under nitrogen pressure which is elevated above atmospheric; and

[0019] (b) thermally exciting a boron-containing target.

[0020] Especially advantageous results are obtained if the boron-containing target is thermally excited by means of a laser, such as a free electron laser or a carbon dioxide laser.

[0021] Beneficial results are obtained if the boron-containing target is made of compressed boron powder or compressed boron nitride powder.

[0022] The target is advantageously cylindrical, rotating, and illuminated on the radius, or cylindrical, rotating, and

illuminated on one face. However, the target may also be stationary. Further preferred target orientation and illuminations are described in greater detail below.

[0023] Highly desirable and very advantageous results are obtained if the process comprises:

[0024] (a) creating a source of boron vapor;

[0025] (b) mixing the boron vapor with nitrogen gas so that a mixture of boron vapor and nitrogen gas is present at a nucleation site, the nitrogen gas being provided at a pressure which is greater than about 2 atmospheres but less than about 250 atmospheres; and

[0026] (c) harvesting boron nitride nanotubes, which are formed at the nucleation site, advantageously in the absence of a catalyst.

[0027] The source of boron vapor is advantageously provided by supplying energy to a solid boron-containing target, such energy being sufficient to break bonds in the solid boron-containing target, thereby allowing boron vapor to enter the vapor state.

[0028] This energy is preferably focused thermal energy. This energy is conveniently and advantageously in the form of a laser beam which is directed at the solid boron-containing target. Exemplary lasers employed to supply such a laser beam beneficially include a free electron laser and a carbon dioxide laser, among others known to the skilled artisan. Other thermal techniques that produce an appropriately shaped boron vapor plume under the elevated ambient nitrogen pressure may also be useful.

[0029] Excellent results have been obtained when the solid boron-containing target is a plug or block of pressed boron powder or pressed boron nitride powder. Moreover, it has been found to be advantageous and convenient if a laser beam, which is directed at the solid boron-containing target, is allowed to bore an depression in the solid boron-containing target as the laser beam is directed thereat, thereby creating a stream of boron vapor by laser heating inside the depression. This stream of boron vapor is allowed to flow upwardly from the bottom of the depression and through the depression, after which it contacts the nitrogen gas. The nitrogen gas is kept under pressure in a synthesis chamber which encloses the solid boron-containing target and contains the nitrogen gas under pressure.

[0030] Although nitrogen gas may be advantageously employed at a pressure greater than about 2 atmospheres but less than about 250 atmospheres, very excellent results are achieved if nitrogen gas is provided at a pressure from greater than about 2 atmospheres up to about 12 atmospheres.

[0031] Boron nitride nanotubes as described herein are formed according to the present invention at a nucleation site, preferably in the absence of a catalyst. The nucleation site is advantageously a surface, especially a surface having an asperity. It has been found to be very beneficial if the nucleation site is the upper periphery of the indentation in the solid boron-containing target, where any asperity exists. Boron nitride nanotubes are formed at this nucleation site and propagate away therefrom in the direction of flow of the stream of boron vapor, which stream has been created by heating within the indentation.

[0032] After they are formed, the boron nitride nanotubes are harvested, advantageously continuously, by standard means known to the skilled artisan. As an example of such continuous harvesting, a growth rate of about 10 cm/sec for the boron nanotubes has been achieved by the present process. A suitable, but not exclusively useful, harvesting process and apparatus are described below in connection with the description of the apparatus depicted in FIG. **1**.

[0033] By the present process, boron nitride nanotubes are produced which are crystalline nanotubes having continuous, parallel, substantially defect-free and sp2 bonded walls. These nanotubes are single, double, few, and/or multi-walled nanotubes. Highly preferred nanotubes prepared in accordance with the present invention have elongated lengths with inside diameters of between about 1.5 and about 2.5 nanometers and tubular walls having a thickness of at least one molecule boron nitride. Typical such nanotubes are shown in the schematic representation of transmission electron microscope photos of single and multi-walled nanotubes prepared in accordance with the present invention as schematically shown in FIG. **4**.

[0034] Under elevated ambient pressure (e.g., ~12 bar (1.2 MPa), and with the appropriate feedstock, few-walled boron nitride nanotube (FW-BNNT) fibrils will grow continuously by surface nucleation from seemingly arbitrary asperities at a high linear rate (at least 10 per second). These fibers or fibrils are referred to as "streamers" because they appear to follow the streamlines of the vapor flow in the synthesis chamber, flapping in a motion reminiscent of a kite tail.

[0035] As described in International Publication No. WO 2009/017526, a preferred heating source comprising a laser beam comprising a 1.6 micron wavelength, 8 mm diameter, unfocused, 1 kW, beam from a FEL (free electron laser), propagates vertically downward into the target. The target, according to this example, a 2.5 cm diameter plug of pressed boron metal powder rotates on a turntable at 20 sec/revolution. The center of rotation of the target is offset by about a half beam diameter from the center of the beam, so that the laser drills or bores a depression about twice its diameter as the target spins. An ambient temperature elevated pressure nitrogen gas is fed into the synthesis chamber continuously.

[0036] At the periphery of the laser-bored depression, streamers form and are elongated by the upward flow of boron vapor. The flapping motion occurs as the fibers/fibrils follow the streamlines of the turbulent boron vapor flow. The boron vapor is created by laser heating at the bottom of the indentation. Streamers form quickly, reaching over a centimeter in length within about $\frac{1}{30}^{th}$ of a second. Sections of streamers snap off and swirl above the target before being carried from the chamber by the apparatus described hereinafter. Elevated chamber nitrogen pressure is critical to the formation of streamers. When the nitrogen pressure is reduced from, for example, 12 bar to slightly above 1 bar (near atmospheric), no streamers are seen, and instead, a shower of sparks is ejected from the laser illumination zone. In post-run analysis, the sparks appear to be droplets of boron metal that has solidified after ejection from the laser impact/illumination zone, and come to rest in the bottom of the chamber. An odor of boron vapor is present when the synthesis chamber is opened, indicating a lack of reaction with nitrogen.

[0037] Streamers are collected from both the target face and downstream on collector surfaces (described below). When held by its ends, a streamer feels like a piece of spider silk, and is similar thereto in appearance, medium matte grey in color. It can be plucked like a guitar string to two or three times its length and then returns to its original shape.

[0038] This behavior is explained in greater detail and more fully in connection with a number of photomicrographs presented in aforementioned International Publication WO 2009/017525.

[0039] At this point, a significant upward flow of boron vapor is established. Based on post-run analysis of the target, the streamers appear to form according to the aerodynamic mechanism described in greater detail below.

[0040] As described in International Publication WO 2009/017525 at the base of each long streamer, many shorter individual BNNT feeder roots are seen. It is concluded that these short roots tangle together after growing a few millimeters, due to the turbulent forces of the upward heating-induced boron vapor flow. The main streamers grow to a multi-centimeter length, fed by the fast mutual growth of their feeder roots. Examination under optical and SEM microscopes shows that individual roots are attached to a variety of asperities on the surface: grain boundaries in the solidified boron metal, micron-sized droplets on the surface, and white particles of apparent boron nitride crystals.

[0041] Because the multi-centimeter-long fibers tangle after the laser is shutdown, it is not possible to photograph full-length streamers in their extended condition. However, several streamers in the early stages of BNNT growth (feeder roots) are seen along the periphery of the target and have been photographed with an optical microscope as shown in FIG. 5 of aforementioned International Publication WO 2009/017525.

[0042] Based on these observations, it is concluded that unlike the formation of carbon nanotubes, boron nitride nanotubes do not require a chemically catalytic surface for nucleation. They will simply form spontaneously and continuously by root growth on any suitable surface, e.g., an asperity in a zone where hot boron vapor and cold nitrogen gas mix to the correct stoichiometry. Under the elevated pressure employed, the growth rate is centimeters (preferably at least 10) per second in a localized fiber/fibril.

[0043] Based on these observations it appears that BNNT production is fundamentally less complicated than carbon nanotube (CNT) production where a gas-borne cloud or coated surface of catalytic particles must be produced and kept active during the growth process.

[0044] It is important to note that the laser is only one means of heating powdered boron metal to create boron vapor. The heating zone and BNNT formation zone are physically separated. Although the laser-boring mechanism that forms the depressions in this implementation may be unique to the FEL beam properties, the technique is applicable with other lasers and other sources of heat given an appropriate geometry. There are, of course, substantial engineering obstacles, as the boiling point of boron, for example, at 12 bar is high (3250 C). This temperature is readily accessible to laser and arc heating. Other heating methods that can achieve the appropriate temperatures and generate the flow of boron vapor from the depression should be equally effective.

[0045] Thus, the method of the present invention entails vaporizing boron under high pressure and impinging the resultant buoyant plume of gaseous boron on a condenser, initiating the formation of BNNTs. The technique is fast and scalable, seemingly dependent only on the rate at which boron can be vaporized in the chamber. Previous work reviewed the limited success of BNNT synthesis techniques available to date, i.e. those using: arc discharge, laser vaporization, chemical vapor deposition, chemical reaction, and atomic deposition. The current technique is most closely related to 'laser vaporization' but introduces the use of forced condensation (a new growth mechanism) and operates in an unexplored range of pressure.

[0046] Our technique uses laser heating to create boron vapor, but the method is not a 'laser' method per se. The type of heating source, in this case a laser, is not critical. The growth zone is physically isolated from the heating zone, near or on a separate condenser surface. The technique works equally well with the two heat sources currently available to us, a near-infrared free electron laser and a far infrared commercial metal-cutting laser.

[0047] To produce the fibrils of the present invention, a high power laser is used to boil boron in a high pressure nitrogen environment within a chamber as described more fully below. The high ambient pressure produces a large density ratio between the boron vapor plume and the nitrogen and thus a strong buoyancy force that accelerates the boron vapor vertically towards the ceiling of chamber. The growth of the fibrils initiates when the boron vapor plume crosses the condenser and rapidly proceeds towards the ceiling of the chamber. Flow visualization indicates that 10 cm of growth often occurs within a single video frame, less than 33 milliseconds, indicating a growth rate equal to or greater than 3 meters per second. Fibrils on the order of ~1 mm in diameter have been observed under these fabricating conditions. Such fibrils comprise a bunch or collection of parallel oriented BNNTs distinct vertical strands which extend the full height of the image indicating that the material has an alignment axis parallel to the growth direction. Along the growth axis, the material can be stretched elastically like a cobweb. Transverse to the growth axis, the material can easily be separated into individual strands with the fingers. On the micron and submicron scale, the structure is a network of long, branching nanotubes and tube bundles, often linked at nodes. SEM showed that the nodes were primarily nano-droplets of boron, coated with layers of boron nitride.

[0048] A yarn can be spun from a mass of raw BNNT fibrils grown as described herein. Such a yarn is fabricated from a collected mass of fibrils as shown/depicted in FIG. **2**. This mass of about 60 mg, with the appearance and texture of a soft elongated cotton ball, is the raw product of a 30 minute production run. A group of fibrils weighing about 10 mg (representing 5 minutes of synthesis time) was separated from the mass, drawn in the growth direction, i.e. lengthwise, and finger-twisted to form a simple one-ply yarn (see FIG. **3**) with a twist angle of about 45 degrees. Before twisting, the fibrils were delicate to the touch with little mechanical strength, but as a spun yarn could support a load, demonstrating the improved strength obtained due to spinning. The yarn in FIG. **3** had a relatively large diameter of about 1 mm, was loosely packed, and was spun dry from unwashed raw material—all unfavorable conditions for mechanical strength. This implies that the underlying staple fibers (BNNT bundles/fibrils) are relatively long to counteract these disadvantages and that considerable improvement in strength can be expected with more refined spinning processes.

[0049] Referring now to accompanying FIG. **1**, an apparatus **10** useful in the production of BNNT fibrils in accordance with the present invention comprises: a pressure chamber **12** containing; a continuously fed or rotated boron nitride target **14**; a source of thermal energy preferably a focused laser beam **16**; a rotating cooled condenser ring **18**; a source of pressurized nitrogen gas **20**; and a mechanism **22** for extracting boron nitride nanotubes from pressure chamber **12** after boron nitride vaporized by the thermal energy source forms a boron nitride plume **24** that condenses on or in the vicinity of rotating cooled condenser ring **18**.

[0050] As shown in accompanying FIG. **1**, thermal energy source **16** is preferably a laser beam introduced into pressure chamber **12** via a convex lens **26** that allows for focusing of laser beam/thermal energy source **16** within pressure chamber **12**. Also as shown in FIG. **1**, cooled condenser ring **18** is rotated continuously by virtue of its being mounted on a rotating shaft **28** such that a new surface thereof is constantly being brought into the proximity of mechanism **22**, in the embodiment shown in FIG. **1**, a condenser tube **22**.

[0051] In the preferred embodiment depicted in FIG. **1**, boron nitride target **14** is a commercially available hot pressed hexagonal boron nitride rod **14** that is continuously fed into the field of laser beam **16** by a motor driven plunger rod, rotator or similar device **30**. According to a preferred embodiment, boron nitride target **14** is of square cross-section about 0.050" on a side and is introduced into laser beam **16** not at the focal waist of laser beam **16** but rather at a position where laser beam **16** is of approximately the same size as boron nitride target rod **14**. According to this preferred embodiment, target rod **14** is advanced at a rate of about 1 mm/sec into the beam **16** of a 2 kW CO_2 laser having a wavelength of about 10.6 microns and a diameter of about 12 mm.

[0052] A small flow of nitrogen gas is of about 40 SCFH is maintained into pressure chamber **12** via nitrogen feed **20** whose flow is regulated, for example, by a needle valve **32** in the chamber exhaust **34**.

[0053] According to the preferred embodiment depicted in FIG. **1**, laser beam **16** terminates in a copper block **38** cooled by water provided thereto by inlet and outlet **38** and **40**. Copper block **38** is designed to absorb the full, continuous power of laser beam **16** without damage.

[0054] Similarly, rotating condenser **18** is water cooled by conventional means well within the skills of the skilled artisan to maintain it a temperature of about 20° C. According to the preferred embodiment depicted in FIG. **1**, rotating condenser **18** is a hoop of about 0.025" copper attached to a water cooled rotating copper shaft **28** although other materials such as stainless steel, tungsten, niobium, hot pressed boron nitride, boron powder, boron castings etc. are similarly useful.

[0055] In operation, as target rod **14** is converted continuously from solid to vapor by the action of laser beam **16**, a buoyant plume of vapors **24** rise vertically from the laser interaction zone. Plume **24** is intercepted by condenser ring **18**. Where plume **24** is intercepted by condenser ring **18**, boron nitride nanotubes form at a high rate. Web-like tufts of boron nitride nanotube fibrils up to 4 inches in length and more, form in vertical structures which are attached at the lower end to condenser ring **18**. These boron nitride nanotube structures form in fractions of a second, as recorded by videographic visualizations. As condenser ring **18** rotates, fresh boron nitride nanotubes grow on each newly exposed section of the advancing condenser surface.

[0056] The boron nitride nanotube fibrils are removed from rotating condenser **18** by means of a collection tube **22** which leads to the outside of pressure chamber **12**. When a ball valve (not shown) in collection tube **22** is opened, the boron nitride nanotube fibrils are "vacuumed" from rotating condenser ring **18** by the nitrogen gas exhausting to 1 atmosphere. Boron nitride nanotube fibrils can be collected, for example, in a wire mesh filter installed in-line in collection tube **22** (not shown) or simply spun into yarn as they exit collection tube **22**.

[0057] While the foregoing describes a specifically preferred apparatus for obtaining the materials of the present invention, it will be apparent that other variations of the particular parameters can be utilized. For example: hot-pressed boron nitride was used as the preferred target, but other targets will be suitable, given acceptable interaction with the laser. For instance, hot pressed boron powder has been produced in the literature and would make a good target, given the appropriate laser properties. Any dense version of boron or boron nitride will work; as long as the laser interacts with the target to produce a continuous stream of vapor. The wavelength or other laser properties are not important. Any kW class laser should reproduce these results. Nd:YAG, or free electron lasers are 2 examples; the shape of condenser **18** can take many variations as long as it provides for free flow of the vapor plume it will work and Nb wire, W wire, Nb sheetstock, and Cu sheetstock have all proven useful; both mechanical and suction have been shown as useful to collect boron nitride nanotubes. Since the material tends to stick to itself or to a surface, it can be wrapped around, stuck to, or sucked into any number of geometries and since boron nitride nanotubes also responds well to static charging they can be collected by this mechanism as well. Additionally, although the cooled condenser has been depicted as a cooled ring, it could equally as well comprise a cooled oscillating structure and the mechanism for collecting boron nitride nanotubes could comprise one or more collection tubes in the vicinity of the extremes of oscillation of the cooled oscillating condenser.

[0058] Thus, highly crystalline, long, BNNTs, BNNT fibrils, BNNT bundles of fibrils—sufficiently long to spin directly into yarn—have been grown for the first time. They are high-aspect ratio nanotubes with straight parallel walls and few defects and are therefore anticipated to fully embody the many desirable material properties predicted by theory. They grow without catalyst or additives and at high linear rates (meters per second) suggesting a promising and environmentally favorable means of manufacture.

[0059] As the invention has been described, it will be apparent to those skilled in the art that the same may be varied in many ways without departing from the spirit and scope thereof. Any and all such modifications are intended to be included within the scope of the appended claims.

What is claimed is:

1) Boron nitride nanotube fibrils comprised of longitudinally aligned bundles of boron nitride nanotubes 20 μm or more in length.

2) The boron nitride nanotube fibrils of claim **1** wherein the longitudinally aligned bundles of boron nitride nanotubes are at least 10 cm long.

3) The boron nitride nanotube fibrils of claim **1** wherein the boron nitride nanotubes are single walled, few walled or multi-walled.

4) A boron nitride yarn comprising spun boron nitride nanotube fibrils comprised of longitudinally aligned bundles of boron nitride nanotubes 20 μm or more in length.

5) The boron nitride yarn of claim **4** wherein the longitudinally aligned bundles of boron nitride nanotubes are at least 10 cm long.

6) The boron nitride yarn of claim **4** wherein the boron nitride nanotubes are single walled, few walled or multi walled.

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