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(54) **METHOD FOR PRODUCING NANO-STRUCTURED MATERIALS**

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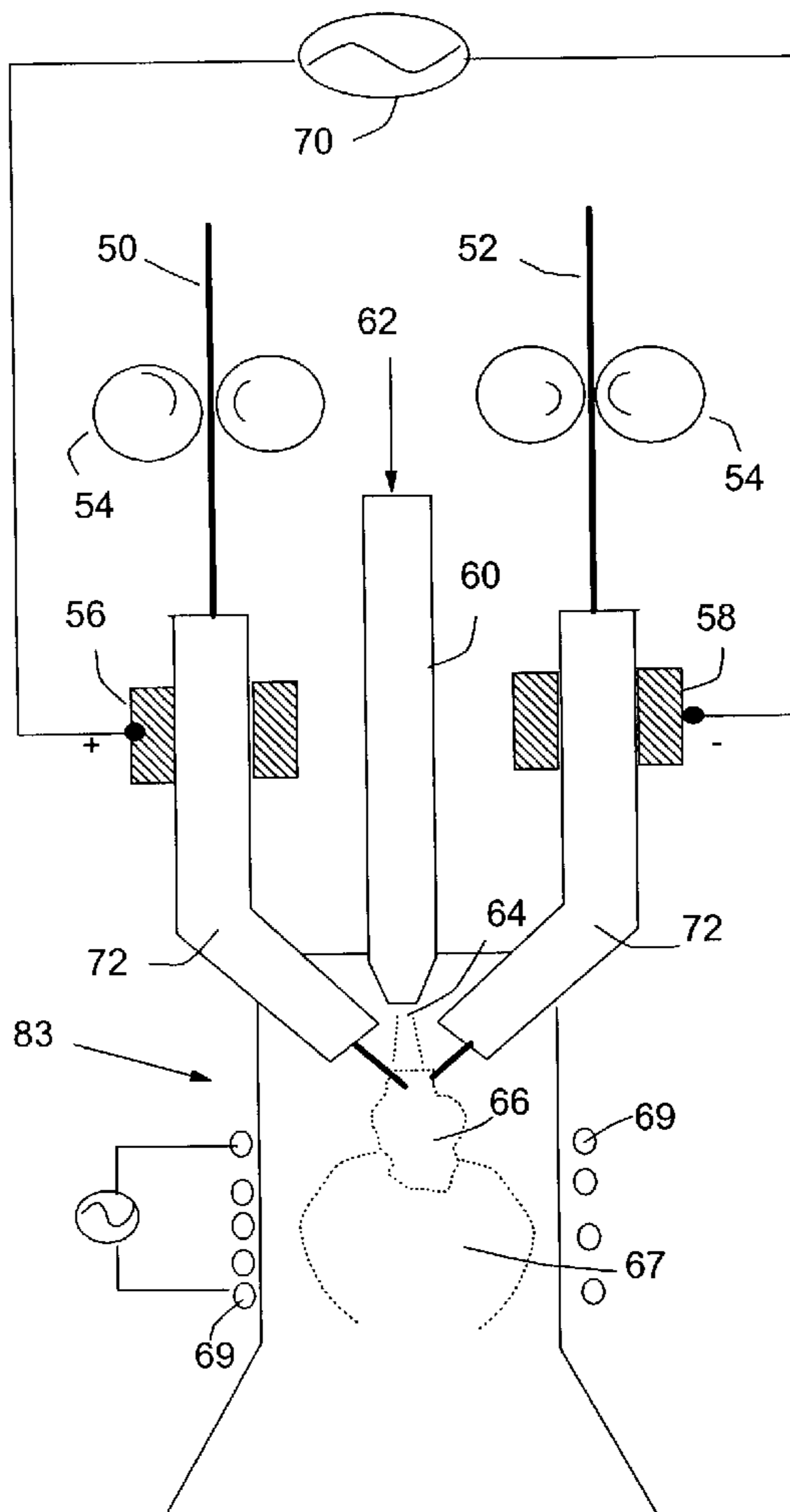
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(57) **ABSTRACT**

A method for synthesizing a nano-structured material, including four primary steps: (A) providing a reaction

chamber wherein the nano-structured material is generated from at least a starting material selected from the group consisting of a metal, a metal alloy, a metal compound, and a ceramic; (B) operating a twin-wire arc nozzle, comprising two wires and a working gas being controllably fed into the chamber, to form an arc between two converging leading tips of the two wires to heat and melt the starting material at the leading tips for providing a stream of liquid droplets traveling in a predetermined direction (preferably vertically downward); (C) operating at least a second high energy source for producing a vaporizing zone adjacent to the arc and inside the chamber wherein the liquid droplets are vaporized to form vapor species; and (D) cooling the vapor species for forming the nano-structured material. The second high energy source is selected from the group consisting of a laser beam, an electron beam, an ion beam, a flame, an induction plasma, and combinations thereof. The second high energy source may also be a plurality of arc plasmas. The nano-structured material produced can be in the form of a nanometer-sized powder particles or a coating (or thin film) containing nanometer-sized phases deposited on a substrate.



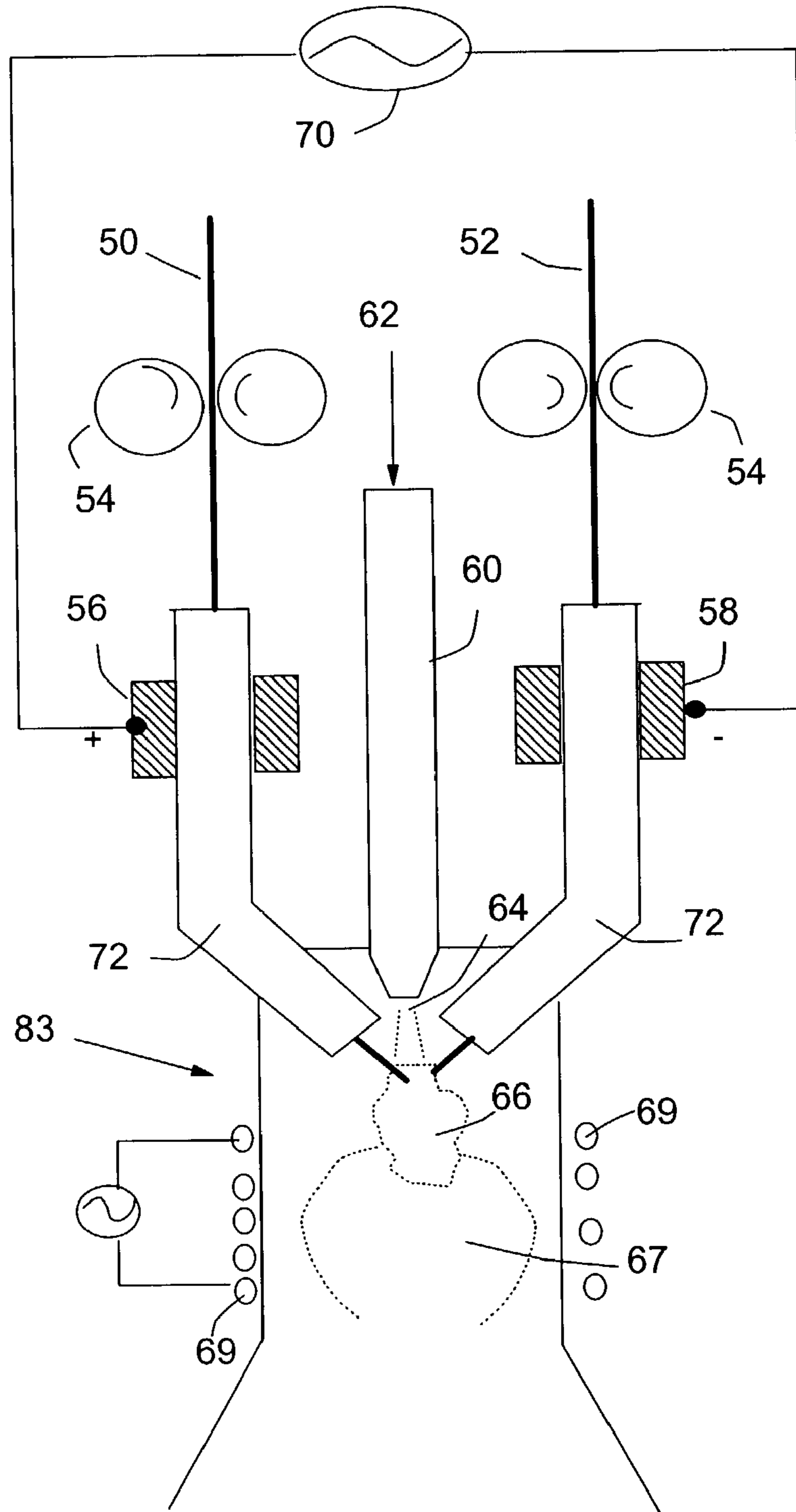


FIG.1

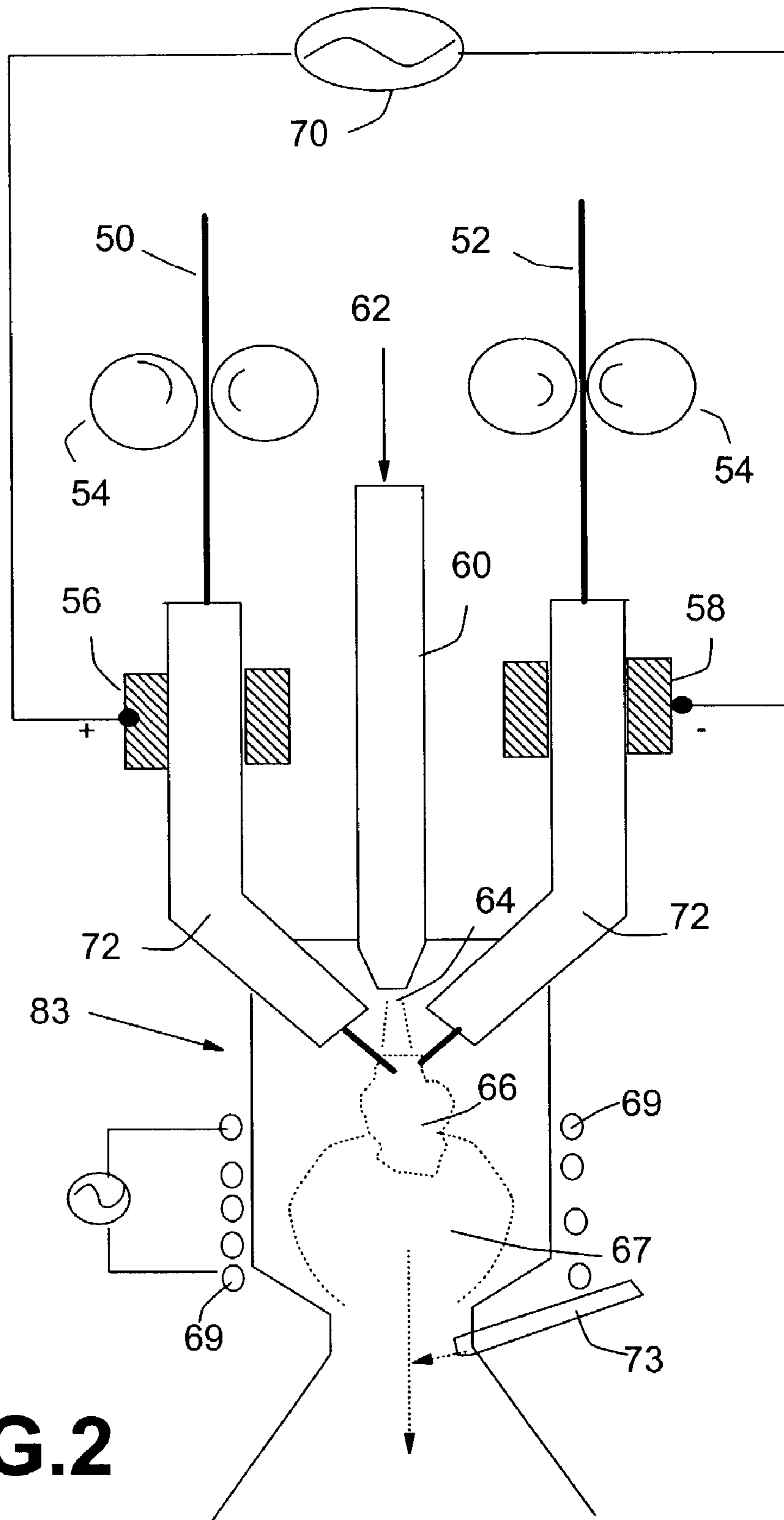


FIG.2

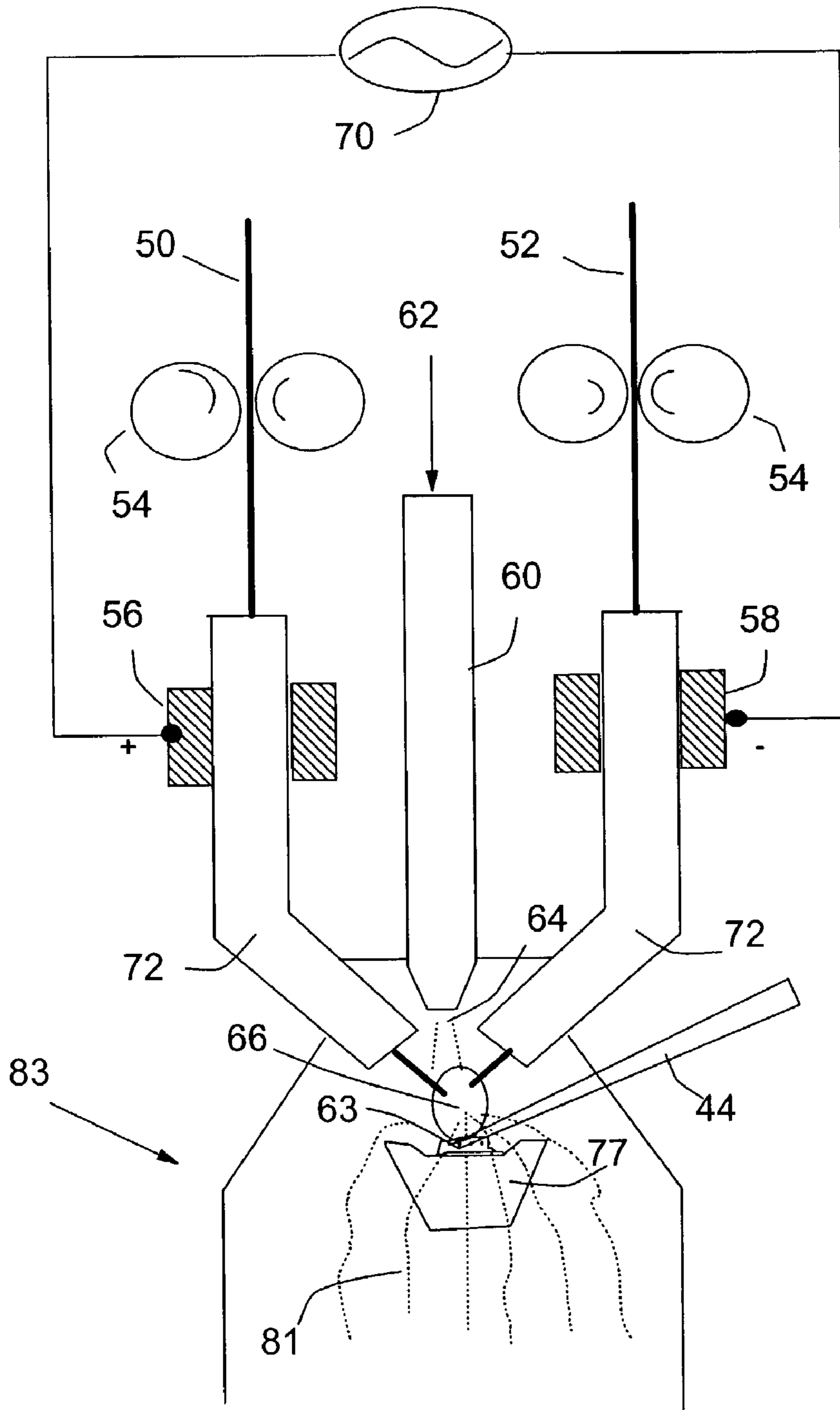


FIG.3a

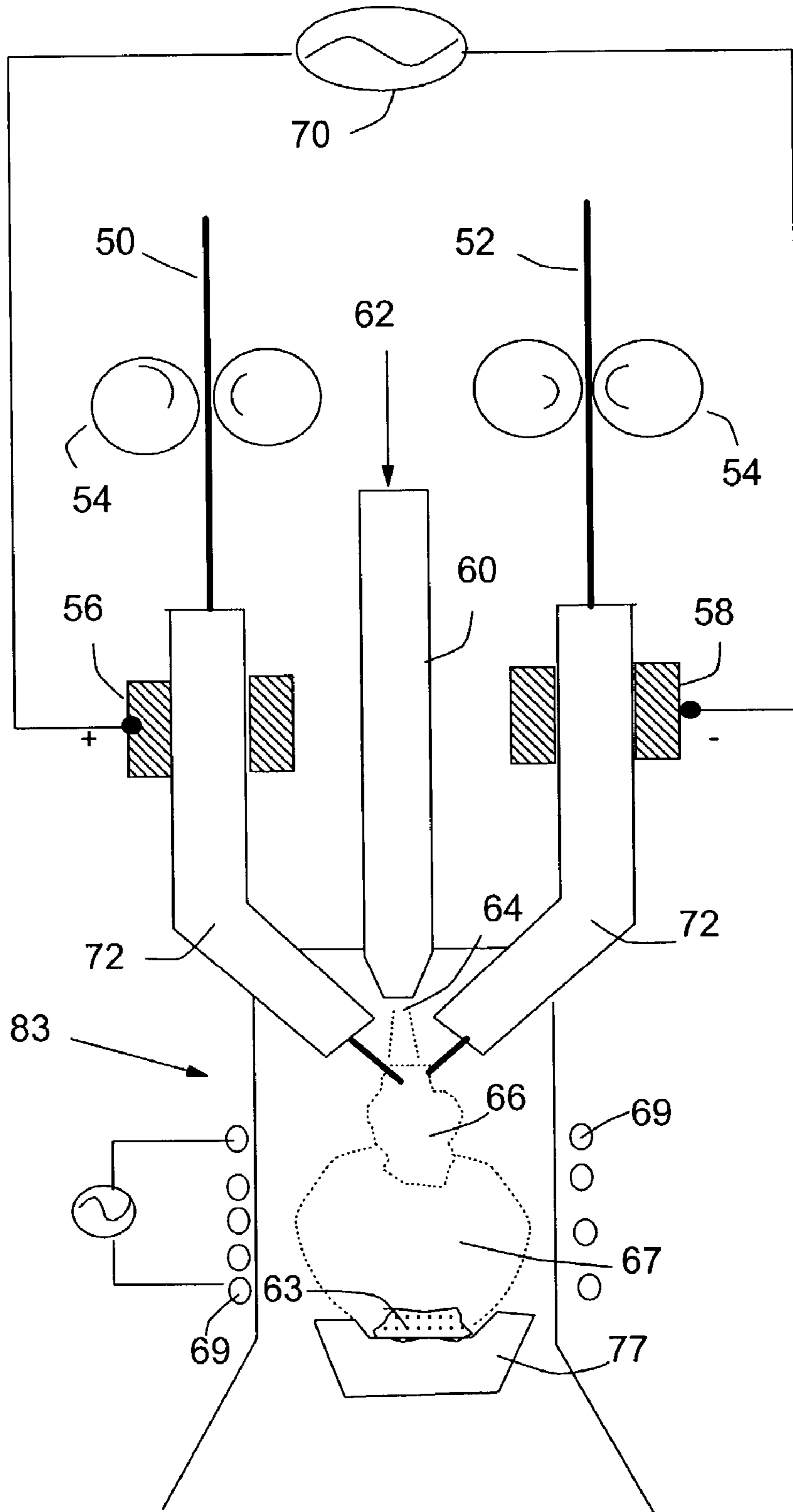
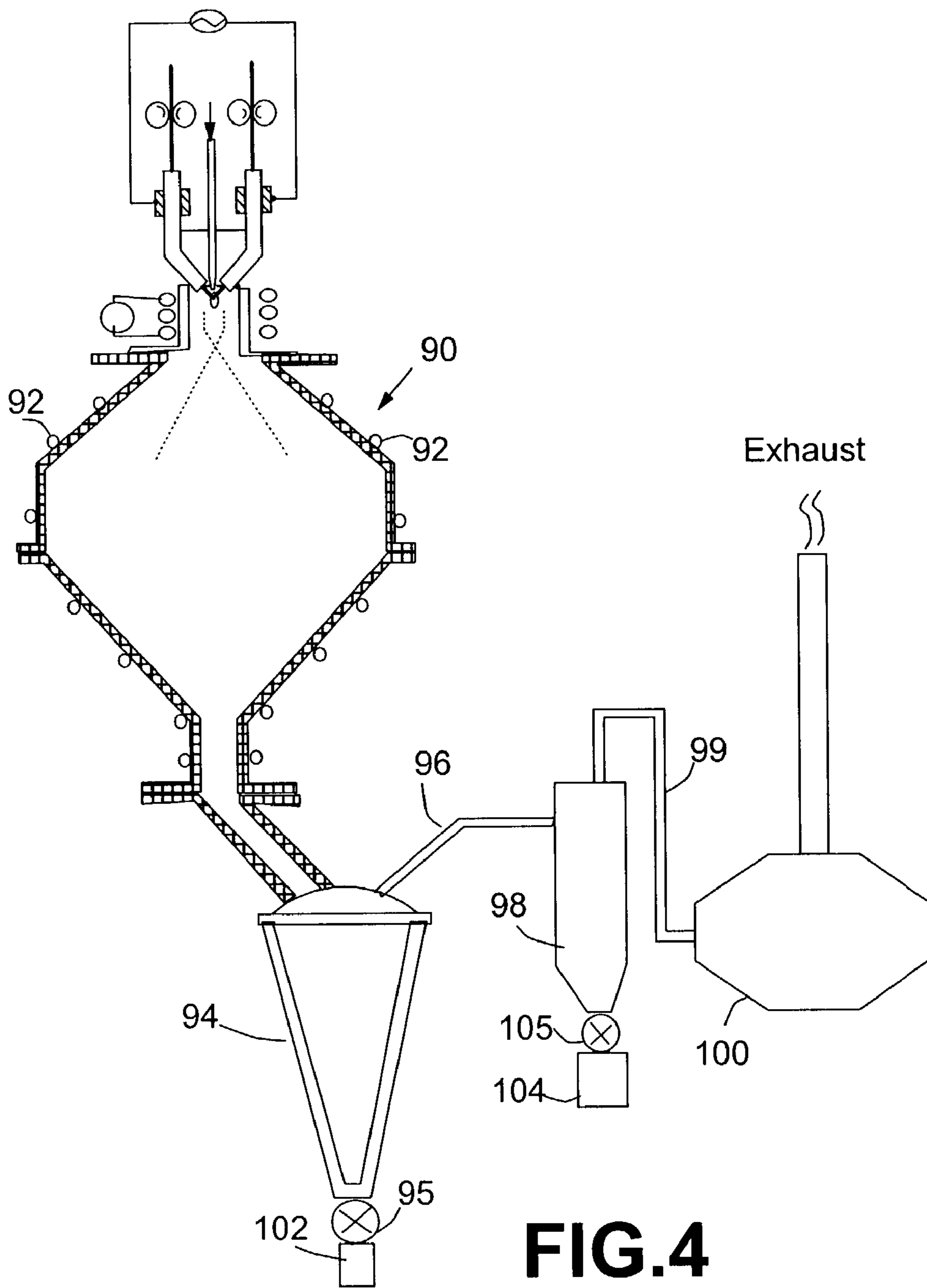


FIG.3b



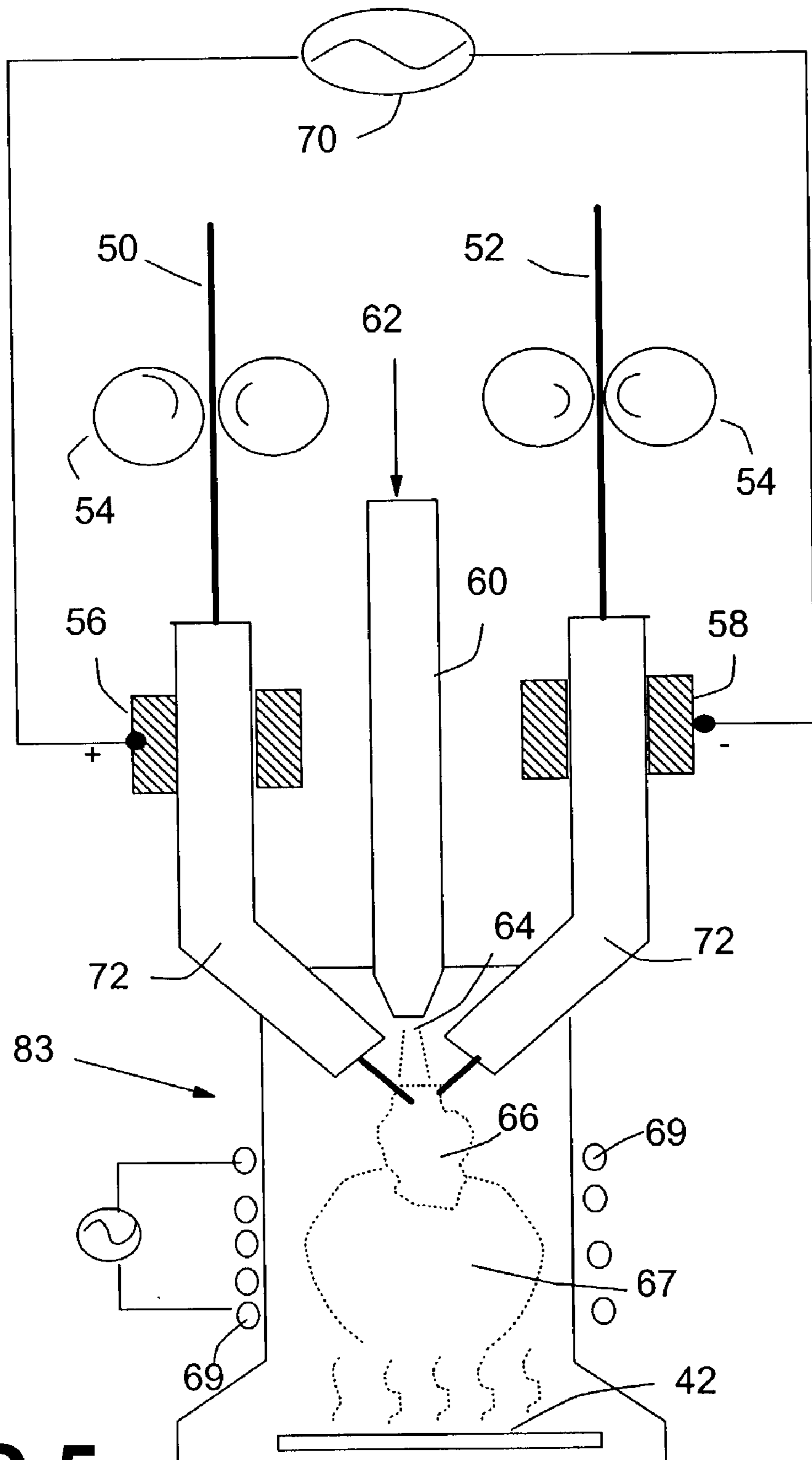


FIG. 5

METHOD FOR PRODUCING NANO-STRUCTURED MATERIALS

[0001] The present invention was based on the research results of a project supported by the U.S. National Science Foundation SBIR Program. The U.S. Government has certain rights on this patent.

FIELD OF THE INVENTION

[0002] The present invention relates to a method for producing nano-structured material, including nanometer-sized powder particles and a coating or thin film containing nanometer-sized phases from a starting material such as a metal, metal alloy, metal compound, and ceramic. More particularly, it relates to a method for producing nano-structured materials at a high production rate using a twin-wire arc based device for material feeding, heating and melting along with at least a second energy source for heating and vaporizing.

BACKGROUND

[0003] Nanometer-sized particles and phases ($d \leq 100$ nm) of metals, semiconductors and ceramics exhibit unique processing characteristics as well as performance properties. The novel properties of nano-structured materials are due to their small residual pore sizes (small intrinsic defect sizes), limited dimensions of grains, phases or domains, unique Bohr radius, and large fraction of atoms residing at the interfaces or grain boundaries. Specifically, ceramics fabricated from ultra-fine particles are known to possess high strength and toughness because of the ultra-small intrinsic defect sizes and the ability for grain boundaries to undergo a large plastic deformation. In a multi-phase material, limited phase dimensions could imply a limited crack propagation path if the brittle phase is surrounded by ductile phases so the cracks in a brittle phase would not easily reach a critical crack size. In addition, dislocation movement distances in a metal could be limited in ultra fine metallic phases or grains, leading to unusually high strength and hardness. Even with only one constituent phase, a nano-structured crystalline material may be considered as a two-phase material, composed of distinct interface and crystalline phases. Further, the possibilities for reacting, coating, and mixing various types of nano materials create the potential for fabricating new composites with nanometer-sized phases and novel properties. Commercial applications of nano particles have included health care/cosmetics, chemical catalysts, microelectronic devices, polishing slurries, light-emitting devices, structural ceramics, and biomedical devices.

[0004] The techniques for the generation of nanometer-sized particles and nano-phased films or coatings may be divided into three broad categories: vacuum, gas-phase, and condensed-phase synthesis. Vacuum synthesis techniques include sputtering, laser ablation, and liquid-metal ion sources. Gas-phase synthesis includes inert gas condensation, oven sources (for direct evaporation into a gas to produce an aerosol or smoke of clusters), laser-induced vaporization, electron beam-induced vaporization, laser pyrolysis, aerosol decomposition and flame hydrolysis. Condensed-phase synthesis includes reduction of metal ions in an acidic aqueous solution, liquid phase precipitation of semiconductor clusters, and decomposition-precipitation of

ionic materials for ceramic clusters. Other methods include high-energy milling, mix-alloy processing, chemical vapor deposition (CVD), and sol-gel techniques.

[0005] All of these techniques have one or more of the following problems or shortcomings:

[0006] (1) Most of these prior-art techniques provide extremely low production rates. It is not unusual to find a production rate of several grams a day. Vacuum sputtering, for instance, only produces small amounts of particles at a time. Laser ablation and laser-assisted chemical vapor deposition techniques are well-known to be excessively slow processes. The high-energy ball milling method, known to be a "quantity" process, is capable of producing only several kilograms of nano-scaled powders in approximately 100 hours. These low production rates, resulting in high product costs, have severely limited the utility value of nano-phase materials. There is, therefore, a clear need for a faster, more cost-effective method for preparing nanometer-sized powder materials and nano-phased coatings.

[0007] (2) Condensed-phase synthesis such as direct reaction of metallic silicon with nitrogen to produce silicon nitride powder requires pre-production of metallic silicon of high purity in finely powdered form. This reaction tends to produce a silicon nitride powder with a broad particle size distribution. Furthermore, this particular reaction does not yield a product powder finer than 100 nm except with great difficulty. Due to the limited availability of pure metallic silicon in finely powdered form, the use of an impure metallic powder necessarily leads to an impure ceramic product. These shortcomings are true of essentially all metallic elements, not just silicon.

[0008] (3) Some processes require expensive precursor materials to ceramic powders and could result in harmful gas that has to be properly disposed of. For instance, the reaction scheme of $3\text{SiCl}_4 + 4\text{NH}_3 = \text{Si}_3\text{N}_4 + 12\text{HCl}$ involves the utilization of expensive SiCl_4 and produces dangerous HCl gas.

[0009] (4) Most of the prior-art processes are capable of producing a particular type of metal, metal compound, or ceramic powder at a time, but do not permit the preparation of a uniform mixture of two or more types of nano-scaled powders at a predetermined proportion.

[0010] (5) Most of the prior-art processes require heavy, complicated, and/or expensive equipment, resulting in high production costs.

[0011] (6) The conventional mechanical attrition and grinding processes have the disadvantages that powders can only be produced up to a certain fineness and with relatively broad particle-size distribution. As a matter of fact, with the currently familiar large-scale process for manufacturing powders it is rarely possible, or only possible with considerable difficulty, to produce powders having average particle sizes of less than 0.5 μm (microns).

[0012] (7) Aerosol processes provide the advantages of small particle size, narrow size distribution, nearly spherical particles and high purity. Aerosol processes also are energy efficient and avoid the treatment of

large liquid volumes associated with traditional wet chemistry processes. However, conventional aerosol processes are very complex and involve many physicochemical phenomena and mechanisms, such as chemical reaction, particle nucleation, condensation, coagulation, aggregation, heat and mass transfer, and thermophoresis. The fundamentals of these processes are not well understood and, consequently, the processes are difficult to control precisely. This makes design, operation and control of industrial reactors to carry out these processes more of an art than a science, relying heavily on experience and empiricism. The most serious problem associated with aerosol decomposition is the formation of impurities from the precursor chemical species (e.g., SiCl_4 , NH_3 , TiCl_4 , etc.). The final impure products cannot be used in health care or cosmetics markets, for instance.

[0013] Ultra-fine particles of metals, metallic compounds, and ceramics can be produced by heating and vaporizing a starting material with a plasma or a multiplicity of plasmas. The thermal plasma approach has a major advantage in that ultra-high temperatures can be readily achieved in relatively large energy amounts. However, in the case of using a direct-current (DC) plasma alone (e.g., in a flame spray apparatus), melting is possible but vaporization of the whole starting material is difficult. In the case of using a high-frequency induction plasma alone, there have been encountered several difficulties: incomplete vaporization, difficulty in maintaining a stable plasma when the starting material is being added to the plasma, and difficulty in feeding the starting powder material into the central portion of the plasma without powder particles being scattered around or dispersed outwardly to adhere to the walls of the plasma chamber. With a hybrid plasma consisting of one DC plasma and one high-frequency plasma, entry of a starting powder material to the DC plasma and then the high-frequency plasma has been difficult.

[0014] In order to overcome this difficulty, Saiki, et al. (U.S. Pat. No. 4,812,166, Mar. 14, 1989) developed a method that involved vaporizing a starting material by supplying this material into a plurality of DC plasma currents combined at the central axis of a work coil for generating a high frequency induction plasma positioned below the DC plasma-generated zone. One major shortcoming of this process is the need to use a complicated configuration of multiple plasmas for heating and vaporizing the incoming material. We have found that, even with such a configuration, it remains difficult for the starting material to enter and stay in both the DC and high-frequency plasmas, leaving a significant portion of the starting material unvaporized and scraped. Furthermore, this process is difficult to control and is not energy efficient since a significant portion of the plasma heat is not utilized.

[0015] Another example of plasma arc-based apparatus is disclosed by Araya, et al. (U.S. Pat. No. 4,732,369, Mar. 22, 1988 and U.S. Pat. No. 4,610,718, Sep. 9, 1986). The apparatus for producing ultra-fine particles by arc energy comprises a generating chamber for generating ultra-fine particles therein, an electrode positioned opposite to a base material so as to generate an electric arc, a suction opening for sucking the particles generated in the chamber, a trap for collecting the particles sucked from the suction opening, and a cooler positioned between the suction opening and the trap

for cooling the sucked ultra-fine particles. The process involves the utilization of dissociable oxygen in the working gas which tends to cause erosion of the non-consumable tungsten electrode used in the apparatus and generates tungsten impurities in the final product. Furthermore, it takes a long time for the base material to vaporize and, hence, the vaporization procedure is a bottle neck in this process, making the whole nano powder production process very slow. Araya, et al. (U.S. Pat. No. 4,619,691, Oct. 28, 1986 and U.S. Pat. No. 5,168,097) used laser beam irradiation or combined laser beam irradiation and arc heating to produce a plume from a base material. Since the base material has to be replenished frequently, this process is non-continuous and not suitable for mass production of nano-scaled powder or nano-phased coating.

[0016] Still another example of a plasma arc-based process for synthesizing nano particles was disclosed by Parker, et al. (U.S. Pat. No. 5,460,701, Oct. 24, 1995 and U.S. Pat. No. 5,514,349, May 7, 1996). The system used in this process includes a chamber, a non-consumable cathode shielded against chemical reaction by a working gas (including an inert gas, but not oxidizing gas), a consumable anode vaporizable by an arc formed between the cathode and the anode, and a nozzle for injecting at least one of a quench and a reaction gas in the boundaries of the arc. This system has several drawbacks. Firstly, the configuration of having a non-consumable electrode and a consumable electrode being paired up to form an arc does not provide efficient vaporization of the consumable electrode. Just like in the apparatus disclosed by Araya, et al. (U.S. Pat. No. 4,732,369), vaporization of the base material takes a long time. Second, the configuration does not permit an efficient use of the plasma arc energy with most of the energy being wasted. Third, since the ionic or plasma arc environment is highly erosive to the non-consumable electrode, it is difficult to maintain a stable arc and the operator has to replace the electrode periodically.

[0017] Glazunov, et al. (U.S. Pat. No. 3,752,610, Aug. 14, 1973) disclosed a powder-producing device that includes a rotatable, consumable electrode and a non-consumable electrode. In a method proposed by Clark (U.S. Pat. No. 3,887,667, Jun. 3, 1975), an arc is struck between a consumable electrode and a second electrode to produce molten metal which is collected, held and homogenized in a reservoir and subsequently atomized to produce powdered metals. Akers (U.S. Pat. No. 3,975,184, Aug. 17, 1976) developed a method for powder production, which entails striking an electric arc between an electrode and the surface of a pool of molten material. The arc rotates under the influence of a magnetic field to thereby free liquid particles from the surface of the pool. The liquid particles are then quenched to become a solid powder material. Uda, et al. (U.S. Pat. No. 4,376,740, Mar. 15, 1983; U.S. Pat. No. 4,482,134, Nov. 13, 1984; U.S. Pat. No. 4,642,207, Feb. 10, 1987; and U.S. Pat. No. 4,889,665, Dec. 26, 1989) taught a process for producing fine particles of a metal or alloy. The process involves contacting a molten metal or alloy with activated hydrogen gas thereby releasing fine particles of the metal or alloy. The method disclosed by Ogawa, et al. (U.S. Pat. No. 4,610,857, Sep. 9, 1986) entails injecting a powder feed material into a plasma flame created in a reactive gas atmosphere. The powder injection rate is difficult to maintain and, with a high powder injection rate, a significant portion of the powder does not get vaporized by the plasma flame.

[0018] In summary, the above prior art plasma-based methods exhibit one or more of the following shortcomings: (1) The powder particles or grains/phases produced tend to be on the micrometer-scaled and particles of 20 nm or smaller are difficult to obtain with some of these prior-art methods; (2) Most of the prior-art systems or apparatus are not energy efficient with most of the plasma arc energy being wasted; (3) It is difficult to feed the starting material into the plasma zone and maintain the material in the plasma zone for complete vaporization, (4) Systems or apparatus that involve a non-consumable electrode are unstable and difficult to control due to the arc-induced erosion on the non-consumable electrode; (5) In most cases, it takes a long time to achieve complete vaporization of the starting material if at all; and (6) In many cases, the need to have a high vacuum and/or the batch-wise material-feeding mechanism make them non-continuous processes that are not amenable to the mass production of nano-structured materials.

[0019] Accordingly, one object of the present invention is to provide an improved method for producing nano-structured metal, metal compound and ceramic materials.

[0020] A specific object of the present invention is to provide a method that is more reliable (e.g., in which it is easier to feed starting materials) and/or more energy-efficient for producing nano-scale powder materials or nano-phased films/coatings.

[0021] Another specific object of the present invention is to provide a method for producing nano-structured materials at a high throughput rate.

[0022] Another object of the present invention is to provide a method for producing ultra fine metal, metal compound, and ceramic powder materials from a wide range of starting materials.

[0023] A further object of the present invention is to provide a method for producing a mixture of ultra fine powder materials which are well mixed at a predetermined proportion.

SUMMARY OF THE INVENTION

[0024] One embodiment of the present invention is a method for synthesizing a nano-structured material. The method includes four primary steps: (A) providing a reaction chamber wherein the nano-structured material is generated from at least a starting material selected from the group consisting of a metal, a metal alloy, a metal compound, and a ceramic; (B) operating a twin-wire arc nozzle, comprising two wires and a working gas being controllably fed into the chamber, to form an arc between two converging leading tips of the two wires to heat and melt the starting material at the leading tips for providing a stream of liquid droplets traveling in a predetermined direction (preferably vertically downward); (C) operating at least a second high energy source for producing a vaporizing zone adjacent to the arc and inside the chamber wherein the liquid droplets are vaporized to form vapor species; and (D) operating heat treatment means to cool the vapor species for forming the nano-structured material. The second high energy source is selected from the group consisting of a laser beam, an electron beam, an ion beam, a flame and combinations thereof. The second high energy source can be a plurality of arc plasmas. The nano-structured material produced can be

in the form of a nanometer-sized powder particles or a coating (or thin film) containing nanometer-sized phases deposited on a substrate.

[0025] The twin-wire arc nozzle is arranged in supplying relation to the receiving reaction chamber for providing melted droplets of the starting material in the chamber. In step (B), this twin-wire arc nozzle includes two wires made up of at least a starting material, each wire having a leading tip and each wire being continuously or intermittently fed into the chamber in such a fashion that the two leading tips are maintained at a desired separation. The nozzle also includes means for providing electric currents and a working gas for creating an ionized arc between the two converging leading tips for melting the starting material to generate a stream of liquid droplets.

[0026] In one preferred embodiment of the present invention, the method further includes an additional step (E), which is carried out after step (C) and before step (D). The step (E) entails introducing a stream of reactive gas into the reaction chamber to impinge upon the vapor species and exothermically react therewith to produce the nano-structured material. In this embodiment, the nano-structured material can include a metal compound or ceramic material. Step (E) could include operating control means for regulating the flow rate of the reactive gas, thereby enabling variations of the particle size or phase size of the nano-structured material. The reactive gas may be selected from the group consisting of nitrogen, phosphorus, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodine, a carbon-containing gas, and mixtures thereof. The working gas may be selected from the group consisting of nitrogen, hydrogen, noble gases and mixtures thereof.

[0027] In another preferred embodiment, the method contains cooling the vapor species in step (D) to become nanometer-sized powder particles, followed by a step (F) which comprises operating a powder collector for collecting the powder particles. The powder collector may include a powder classifier (e.g., cyclones) and a filter. In the case of producing nanometer-sized powder particles, step (D) could include a sub-step of operating means for injecting a cooling gas into the vapor species, thereby minimizing agglomeration of the nanometer-sized powder particles.

[0028] In the presently invented method, the starting material could include two different materials in a wire. The two different materials could make up the two wires in such a fashion that the two wires have different material compositions. The two different materials could include indium and tin and, if oxygen is used as a reactive gas, the resulting nano-structured material would be indium-tin oxide, a material commonly coated onto a glass substrate for liquid crystal display applications. The two different materials could include antimony and tin.

[0029] In another preferred embodiment, the method further includes a step of positioning a reservoir at the bottom portion of the twin-wire arc or a distance below the twin-wire arc in such a fashion that the reservoir receives the stream of liquid droplets from the wires and further exposes the liquid to a second energy source to vaporize at least a portion of the liquid. Preferably, the second energy source is such that the liquid is completely vaporized.

[0030] The presently invented method is applicable to essentially all metallic materials (including pure metals and

metal alloys), metal compounds, and ceramic materials. As used herein, the term "metal" refers to an element of Groups 2 through 13, inclusive, plus selected elements in Groups 14 and 15 of the periodic table. Thus, the term "metal" broadly refers to the following elements:

[0031] Group 2 or IIA: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

[0032] Groups 3-12: transition metals (Groups IIIB, IVB, VB, VIB, VIIB, VIII, IB, and IIB), including scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc), rhenium (Re), iron (Fe), ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), platinum (Pt), copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and mercury (Hg).

[0033] Group 13 or IIIA: boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl).

[0034] Lanthanides: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

[0035] Group 14 or IVA: germanium (Ge), tin (Sn), and lead (Pb).

[0036] Group 15 or VA: antimony (Sb) and bismuth (Bi).

[0037] When high service temperatures are not required, the component metal element (in an alloy, compound, or ceramic) may be selected from the low melting point group consisting of bismuth, cadmium, cesium, gallium, indium, lead, lithium, rubidium, selenium, tellurium, tin, and zinc. When a high service temperature is required, a metallic element may be selected from the high-melting refractory group consisting of tungsten, molybdenum, tantalum, hafnium and niobium. Other metals with intermediate melting points such as copper, zinc, aluminum, iron, nickel and cobalt may also be selected.

[0038] Some gases may be selected to passivate the nano-scaled clusters to produce un-agglomerated fine metal or ceramic powders and to prevent oxidation or other undesirable reaction from taking place; e.g., Se vapor may be used to passivate the surface of telluride clusters. The other gases may be used to react with the metal clusters to form nanometer-scale compound or ceramic powders of hydride, oxide, carbide, nitride, chloride, fluoride, boride, iodide, sulfide, phosphide, arsenide, selenide, and telluride, and combinations thereof.

[0039] Specifically, a reactive gas can rapidly react with the metal vapor species to form nanometer-sized ceramic particles (e.g., oxides). If the reactive gas contains a mixture of two or more reactive gases (e.g., oxygen and nitrogen), the resulting product will contain a mixture of two compounds or ceramics (e.g., oxide and nitride). If the metal wire is a metal alloy or mixture (e.g., containing both indium and tin elements) and the reactive gas is oxygen, the resulting product will contain ultra-fine indium-tin oxide particles.

[0040] The reactive gas can undergo a reaction with vaporized metal species at high temperatures in a substantially spontaneous and self-sustaining fashion. The reaction heat released is effectively used to sustain the reactions in an already high temperature environment.

[0041] Advantages of the present invention may be summarized as follows:

[0042] 1. A wide variety of nano-structured metal, metal compound, and ceramic materials can be readily produced using the present method. The metallic element(s) in a starting feed material can be selected from any element in the periodic table that is considered to be metallic. The corresponding partner gas reactants may be selected from, for instance, hydrogen, oxygen, carbon, nitrogen, chlorine, fluorine, boron, and sulfur to form respectively metal hydrides, oxides, carbides, nitrides, chlorides, fluorides, borides, and sulfides and combinations thereof. No known prior-art technique is so versatile in terms of readily producing so many different types of nano-structured metallic, compound, and ceramic materials at a high production rate.

[0043] 2. The wire material may contain an alloy of two or more elements which are uniformly dispersed. When vaporized, these elements remain uniformly dispersed and are capable of reacting with selected reactive gases to form uniformly mixed compound or ceramic powder particles. No post-fabrication mixing is necessary for the purpose of making a nano-phased composite material.

[0044] 3. The method allows a spontaneous reaction to proceed between a metallic element and a reactive gas such as oxygen. The reaction heat released is spontaneously used to maintain the reacting medium in a sufficiently high temperature so that the reaction can be self-sustaining until completion for the purpose of producing a compound or ceramic material. The reaction between a metal and certain reactive gas (e.g., oxygen) can rapidly produce a great amount of heat energy, which can be used to drive other reactions that occur concurrently or subsequently when other reactant elements (e.g., carbon or nitrogen) are introduced.

[0045] 4. The method permits an uninterrupted feed of wires or rods, which can be of great length. This feature makes the process fast and effective and now makes it possible to mass produce nano-structured metal, compound, and ceramic materials cost-effectively.

[0046] 5. The method is simple and easy to operate. It does not require the utilization of heavy and expensive equipment. The over-all product costs are very low.

[0047] 6. The present method fundamentally differs from the method used in U.S. Pat. No. 4,610,718 (Sep. 9, 1986 to Araya, et al.). As indicated earlier, the process of Araya, et al. involves the utilization of dissociable oxygen in the working gas which tends to cause erosion of the non-consumable tungsten electrode used in the apparatus and generates tungsten impurities in the final product. The Araya's apparatus design does not allow an efficient use of the arc energy and it takes an excessively long time for the arc to fully vaporize the feed material. In contrast, the presently invented method only requires the twin wire to be

melted (not necessarily vaporized, although partial vaporization is possible, which is a good feature), the produced melt droplets are then substantially vaporized completely when passing through the second heating/vaporizing stage. The apparatus of Araya, et al. is not equipped with a quench gas for preventing particle agglomeration, nor is it supplied with a reactive gas to react with a metal element in the electrode for producing a compound or ceramic material through a self-propagating reaction.

[0048] 7. The present method has several advantages over the method of Parker, et al. (U.S. Pat. No. 5,514,349, May 7, 1996), which is essentially a variant of the method proposed by Araya, et al. In Parker's method, the configuration of having a non-consumable electrode and a consumable electrode being paired up to form an arc again does not provide efficient vaporization of the consumable electrode. A significant portion of the consumable electrode is just melted and drips down to the surface of a supporting substrate to form a "weld pool" thereon. The consumable electrode (typically a thick rod) cannot be advanced (fed) into the arc zone until most of the material in this pool of molten metal is vaporized, which takes a long time. This bottleneck severely limits the rod-feeding rate and the over-all powder production rate with this system is very low. Further, since the ionic or plasma arc environment is highly erosive to the non-consumable electrode in the Parker's system, it is difficult to maintain a stable arc and the operator has to replace the electrode periodically. In contrast, in our present invention, the two wires can be continuously fed into the heating/melting/vaporization chamber with the leading tips of the wires continuously melted (and partially vaporized) at a high feeding rate for producing nano-structured materials continuously without interruption and at a high throughput rate. The un-vaporized melt droplets are completely vaporized during the second-stage heating.

BRIEF DESCRIPTION OF THE DRAWINGS

[0049] FIG. 1A schematic of a preferred embodiment of a twin-wire arc system for producing nano-structured metallic, metal compound, and ceramic materials.

[0050] FIG. 2A system similar to that in FIG. 1, but has a provision for introducing a reactive or cooling gas to impinge upon the vapor species.

[0051] FIG. 3 The same system as in FIG. 1, but with a melt reservoir 77 to receive or trap melt 63 that drips out of the arc 66 and a laser beam 44 to vaporize the melt 63.

[0052] FIG. 4 The same system as in FIG. 1, equipped with a powder classifier-filter system for collecting the produced nano powders.

[0053] FIG. 5 The same system as in FIG. 1, but has a solid substrate to receive nano-scaled species (cooled vapor species) for forming a coating.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0054] In order to illustrate the basic steps involved in the presently invented method, please refer to FIG. 1, which schematically shows one example of the systems that can be

used to produce a nano-structured material. This system includes four major functional component sub-systems:

[0055] (a) a chamber (e.g., 83) in which a starting material is melted and then vaporized;

[0056] (b) a twin-wire electrode device (arc nozzle) in supplying relation to the chamber. This electrode device includes: (i) two wires 50,52 each made up of a desired starting material, each wire having a leading tip 50a or 52a and each wire being continuously or intermittently fed (e.g., through rotating rollers 54) into the chamber in such a fashion that the two leading tips 50a,52a are converged toward each other and maintained at a desired separation; and (ii) means (e.g., power source 70 through two respective conductive jackets 72 and electrodes 56,58) for providing electric current and a working gas 64 (e.g., from a gas source such as a bottle designated by 62 and through a pipe means 60) for creating an ionized arc 66 between the two leading tips for melting the material at the tips to generate a stream of melt droplets in the chamber;

[0057] (c) a second energy source (e.g., a high-frequency induction plasma 67 produced through electric coils 69) to completely vaporize the liquid droplets for generating vapor species, preferably flowing along a predetermined direction (e.g., vertically downward);

[0058] (d) optional means (e.g. through a pipe 73 in FIG. 2) for injecting a reactive gas into a reaction zone inside the chamber at a point inside the tail end of the plasma zone or downstream from the plasma zone. The reactive gas reacts with the vapor species to produce compound or ceramic particles; and

[0059] (e) means to heat treat the vaporized species (e.g., a cooling chamber 90 with cooling water jackets 92 wrapped around the cooling chamber 90 in FIG. 4) to, for instance, allow for condensation of the vapor species, resulting in the formation of nano-sized powder particles. Alternatively, as shown in FIG. 5, a solid substrate 42 may be positioned down stream from the vapor species, which impinge upon and deposit onto the substrate to form a thin film or coating. The temperature in the direct vicinity of the substrate surface may be regulated in such a fashion that vapor species condense and form a coating containing nano-scaled phases; and

[0060] (f) For the production of nano-sized powder particles, a powder collector system (e.g., including a cyclone or powder classifier, from 94 to 105 in FIG. 4) may be used to collect the nano-scaled powder material.

[0061] Based on this system, the method consists of the following four primary steps: (A) providing a reaction chamber wherein the nano-structured material is generated from at least a starting material selected from the group consisting of a metal, a metal alloy, a metal compound, and a ceramic; (B) operating a twin-wire arc nozzle, comprising two wires and a working gas being controllably fed into the chamber, to form an arc between two converging leading tips of the two wires to heat and melt the starting material at the leading tips for providing a stream of liquid droplets traveling in a predetermined direction (preferably vertically downward); (C) operating at least a second high energy

source for producing a vaporizing zone adjacent to the arc and inside the chamber wherein the liquid droplets are vaporized to form vapor species. The second high energy source may be a laser beam, an electron beam, an ion beam, a flame, a high-frequency induction plasma, and combinations thereof. The second high energy source may also be a plurality of arc plasmas; and (D) operating heat treatment means to cool the vapor species for forming the nano-structured material, which can be in the form of a nanometer-sized powder particles or a coating (or thin film) containing nanometer-sized phases deposited on a substrate.

[0062] For the purpose of clearly defining the claims, the word "wire" means a wire of any practical diameter, e.g., from several microns (a thin wire or fiber) to several centimeters (a long, thick rod). A wire can be supplied from a spool, which could provide an uninterrupted supply of a wire as long as several miles. This is a very advantageous feature, which makes the related powder production process a continuous one.

[0063] In a preferred embodiment of the presently invented method, as indicated in FIG. 1, the twin-wire electrode device used in the method basically contains a twin-wire electric arc spray nozzle, which is mainly comprised of two feed wires 50, 52, a feeding mechanism (e.g., including motorized rollers 54), and a working gas passage or pipe means 60 which directs the flow of a working gas from the supply into a cell near the two respective leading tips of the wires. The two metal wires 50, 52 are supplied with a DC voltage or current (one "+" and the other "-") or a pulsed power through the electrodes 56, 58 to form an arc 66. This arc 66, being at an ultra-high temperature (up to 6,000° C.), functions to melt the wire tips to form a stream of liquid droplets. The stream 64 of working gas passes through the passage means 60 into the arc chamber not only to help generate and maintain the arc 66 but also to carry the liquid droplets downward toward the vaporization zone induced by a second energy source such as an high-frequency induction plasma or a laser beam. The power of this energy source is chosen in such a fashion that the stream of liquid, when passing through the vaporization zone, is completely vaporized. The produced vapor species are preferably directed to flow in a desired direction, vertically downward as shown in FIG. 1. The creation of a plasma zone is well-known in the art. The ultra-high temperature in the plasma (up to as high as 32,000° K) rapidly vaporizes the melt droplets that pass through the plasma zone.

[0064] The vapor species may then be allowed to react with a stream of reactive gas introduced into the reaction chamber through a pipe 73 in FIG. 2. The reaction products are metal compounds or ceramics that are different from the starting material in chemical composition. The reaction products, in vapor and/or liquid states, are nano-scaled clusters. It may be noted that, if the gas coming through pipe 73 in FIG. 2 contains a highly reactive gas such as oxygen, the vapor species can quickly react with oxygen to form nano-sized oxide clusters. Since the oxidation of a metal is normally a highly exothermic process, a great amount of reaction heat is released which can in turn be used to activate, maintain, or accelerate the oxidation reactions of other metal vapors, clusters or droplets. Such a self-sustaining reaction rapidly converts the liquid metal droplets or vapor clusters into nano-scaled metal compound or ceramic particles. Other reactive gases that can be selected include

hydrogen, carbon-containing gas (e.g., CO), nitrogen, chlorine, fluorine, boron, iodine, sulfur, phosphorus, arsenic, selenium, tellurium and combinations thereof.

[0065] The vapor species or nano-scaled clusters thus generated could remain in a vapor or liquid state in which individual clusters could aggregate or stick together if left alone. It is therefore desirable to operate a heat treatment means to help the clusters solidify and remain separated from one another if nano powder particles are the desired final product. In this case, the operation of this heat treatment means may include blowing a quenching gas (e.g., cool, inert gas) to impinge upon the vapors or clusters immediately or soon after the vapors or clusters are formed. The cooling gas may contain a small amount of passivating gas to help stabilize the nano particles against any undesired oxidation or other side reaction. These cooling means may include copper or steel tubing 92 or channels, containing cooling water, that are jacketed around the cooling chamber 90. These powders, along with the residual working gas and cooling gas are transferred through a conduit 20 to a powder collector/separater system (e.g., schematically shown in the lower portion of FIG. 4.

[0066] Alternatively, if the desired final product is a nano-grained or nano-phased thin film or coating on a substrate (42 in FIG. 5), then this substrate may be disposed in a position downstream from the vaporization zone 67. The vapor species or their reaction products with a reactive gas are directed to strike the substrate and get deposited thereon to form a thin film or coating. Prior to impinging upon the substrate these vapor species or nano-scaled clusters may go through a heat treatment zone to reach a desired temperature, which dictates the grain or phase size of the resulting coating.

[0067] The twin-wire arc spray nozzle, originally developed for use in a spray coating process, can be adapted in the present method for providing a continuous stream of liquid droplets flowing into the vaporization zone 67. This low-cost device is capable of readily melting and, if so desired, partially vaporizing the metal wire to a temperature as high as 6,000° C.

[0068] Schematically shown in FIG. 1 is an open-style twin-wire arc spray nozzle that can be used in the practice of the presently invented method. Two metal wires 50, 52 are driven by powered rollers 54 to come in physical contact with two respective conductive jackets 72 which are supplied with "+" and "-" voltage or pulsed power through electrically conductive blocks 56 and 58, respectively. The voltage polarity may be reversed; i.e., "-" and "+" instead of "+" and "-". The voltages come from a DC or pulsed power source 70. The lower ends of the two wires approach each other at an angle of approximately 30-60°. The two ends are brought to contact each other for a very brief period of time. Such a "short circuit" contact creates an ultra-high temperature due to a high current density, leading to the formation of an ionized arc 66. A stable arc can be maintained provided that the current is constantly supplied, a certain level of gas pressure is maintained, and the wires are fed at a constant or pulsating speed. A stream 64 of compressed air, introduced through a gas passage 60 from a gas source (e.g., a compressed air bottle), also serves to carry the stream of liquid downward into the vaporization zone.

[0069] For some materials with a relatively high vaporization temperature or boiling point, and if the working gas

flow rate is relatively high, a certain amount of the wire tip material may not be exposed to the high temperature environment for a sufficiently long duration of time needed for a full vaporization. As a consequence, small melt droplets may drip downward toward the cooling chamber in FIG. 4. One way to overcome this difficulty is to make use of a reservoir (77 in FIG. 3a or 3b) positioned just below the twin-wire arc 66 (FIG. 3a) or near the edge of the high-frequency induction plasma 67 (FIG. 3b) to trap or accommodate the un-vaporized material 63, which will continue to receive heat from the plasma 67 (FIG. 3b) or a laser beam 44 (FIG. 3a) for further vaporization.

[0070] In the actual practice of the present method, the cooling chamber 90 is preferably further connected to a powder collector and separator system, as shown in FIG. 4. As an example, the chamber 90 is connected to a collector chamber 94, commonly referred to as an expansion chamber. The lower part of this expansion chamber 94 has an outlet being communicated to a removable powder collection container 102 through a valve 95. The valve 95 is open during production of the clusters so that powder separated and collected by the chamber 94 can be received and collected in the container 102. The expansion chamber may be allowed to communicate through conduits 96,99 with a series of cyclones (only one cyclone 98 being shown) and a filter device (e.g., including a wet scrubber 100). The finely divided metallic, compound, or ceramic powder product is suspended in reaction product gases as well as excess working gas, hereinafter collectively referred to as product gases or product fluids. The product fluids are removed from the chamber 90 through conduit 96,99 and introduced into cyclones 98 and filter/separator device, in order to separate the solid powder from the product fluids. The nano-sized particles are formed completely in the chamber and since the cluster effluent is rapidly cooled to below the powder forming temperatures substantially immediately, little or no additional ceramic or metal solid formation or individual particle growth occurs outside the chamber.

[0071] A cyclone 98 is normally cooled (e.g., externally water chilled) to cool the powder product. As the product fluids travel through cyclones 98, the powder drops into receiver 104 with the valve 105 being open, while gaseous effluent leaves cyclone 98 through conduit 99 into a solid separation chamber (e.g., a wet scrubber 100). The wet scrubber can be a caustic water scrubber, containing packing of balls, saddles, etc. for greater contact. The scrubber separates the fine solid particles from the gas stream and possibly neutralizes acidic species therein before the gas is discharged to the atmosphere or to a flue. Any additional filtering device such as a bag filter, electrostatic precipitator or other equivalent means for separating suspended solids from a gas may be used. While only one cyclone and one solid separator are shown, more than two can be used. Alternatively, other types of powder collector and/or separator devices may be used. Solid powder collector and solid-gas separator systems are widely available in industry.

[0072] The starting material can be an alloy of two or more elements which are uniformly dispersed. When vaporized, these elements remain uniformly dispersed and are capable of reacting with selected reactive gas to form uniformly mixed ceramic powder particles. No post-fabrication mixing

is necessary for the preparation of a hybrid or composite material.

[0073] The reactive gas can contain vapor, liquid, or solid particles suspended in a carrier gas. A solid reactant in fine powder form requires a carrier gas to carry it into the arc cell. An example is fine carbon powders suspended in either an inert gas (e.g., helium) or reactive gas (e.g., oxygen), depending upon the types of intended ceramic powders to be produced. In the former example, a metal carbide will be produced. The helium gas is used only as a carrier medium. In the latter example, oxygen gas is used to react with metal vapor clusters. If more than two reactant elements are used (e.g., carbon particles suspended in oxygen gas, or a mixture of CO and O₂) more complicated reactions can occur. Under favorable conditions, oxidation of a metal occurs, resulting in the release of a great amount of heat, which can be used to promote the reaction between a metal element (if still available) and carbon. The supply of a vaporized metal element and a mixture of two reactant gases can lead to the formation of a mixture of two compounds or ceramics.

[0074] If the method is used to produce a uniform mixture of ceramics from a metallic alloy, this alloy can be introduced as two wires of identical alloy composition into the twin-wire arc spray nozzle. Alternatively, the two wires may be made up of different metal compositions. For example, a technologically important oxide mixture is indium-tin oxides. This product can be used in a flat panel display technology. In one instance, a tin wire and an indium wire were fed into an arc sprayer nozzle and induction plasma and vaporized. An oxygen flow at a rate of 200 scfm under a gas pressure of approximately 200 psi was used to mix and react with the mixture of metal vapor clusters. Nano-scaled indium-tin oxide particles with an average diameter of 12 nm were obtained. A production rate of 20 kilograms per hour was achieved with a lab-scale apparatus.

[0075] Table 1 gives a list of examples of the nano-structured materials produced by the presently invented method.

TABLE 1

List of nanometer-sized powder (NP) and nano-phased coating (NC) materials produced with selected vacuum or reactive gas condition (working gas = argon).					
Starting Material	Group	Vacuum (NP & NC)	Air (NP)	Oxygen gas (NP & NC)	Nitrogen gas (NP)
Cu	IA	Cu	Cu		
Zn	IIA	Zn	Zn + ZnO	ZnO	Zn
Al	III	Al	Al + Al ₂ O ₃	Al ₂ O ₃	Al + AlN
Sn	IVA	Sn	Sn + SnO	SnO ₂	Sn
Ti	IVB	Ti	Ti + TiO ₂	TiO ₂	TiN
Nb	VB	Nb	Nb	Nb ₂ O ₅	Nb ₄ N ₃
Mo	VIIB	Mo	Mo	MoO ₃	Mo
Mn	VIIB	Mn	Mn	Mn ₂ O ₃	Mn + Mn ₄ N
Fe	VIII B	Fe	Fe + Fe ₂ O ₃	Fe ₂ O ₃	Fe
ZnO		ZnO	ZnO	ZnO	ZnO
ZrO ₂		ZrO ₂	ZrO ₂	ZrO ₂	ZrO ₂ + ZrN
Fe-Ti		Fe-Ti		Fe ₂ O ₃ + TiO ₂	Fe + TiN
Ni-Ti		Ni-Ti		NiO + TiO ₂	Ni + TiN
In-Sn				SnO + In ₂ O ₃	

What is claimed:

1. A method for synthesizing a nano-structured material, comprising:

(A) providing a chamber wherein said nano-structured material is generated from at least a starting material selected from the group consisting of a metal, a metal alloy, a metal compound, and a ceramic;

(B) operating a twin-wire arc nozzle, comprising two wires and a working gas being controllably fed into said chamber, to form an arc between two converging leading tips of the two wires to heat and melt said at least a starting material at said leading tips for providing a stream of liquid droplets traveling in a predetermined direction;

(C) operating at least a second high energy source for producing a vaporizing zone adjacent to said arc and inside said chamber with said liquid droplets traveling into said vaporizing zone and being vaporized therein to form vapor species; and

(D) operating heat treatment means to cool said vapor species for forming said nano-structured material.

2. The method as defined in claim 1, wherein said second high energy source is selected from the group consisting of a laser beam, an electron beam, an ion beam, a flame, a high-frequency induction plasma, and combinations thereof.

3. The method as defined in claim 1, wherein said nano-structured material comprises nanometer-sized powder particles.

4. The method as defined in claim 1, wherein step (D) comprises a sub-step of directing said vapor species to impinge upon a substrate and deposit thereon to form said nano-structured material that is characterized by a coating containing nanometer-sized phases deposited on said substrate.

5. The method as defined in claim 1, wherein said second high energy source comprises a plurality of arc plasmas.

6. The method as defined in claim 1, further comprising an additional step (E), after step (C) and before step (D), said step (E) comprises introducing a stream of reactive gas into said chamber to impinge upon said vapor species and exothermically react therewith to produce said nano-structured material.

7. The method as defined in claim 1, wherein step (B) includes:

operating wire feeding and control means to either continuously or intermittently feed said two wires into said chamber in such a fashion that the two leading tips are maintained at a desired separation; and

operating power supply means to provide currents through said two wires to form said arc with a temperature sufficient for melting said at least a starting material at said leading tips.

8. The method as defined in claim 6, wherein step (E) includes operating means for controlling the flow rate of the reactive gas, thereby enabling change of particle size of the nanometer-scaled powder material.

9. The method as defined in claim 6, wherein said reactive gas is selected from the group consisting of nitrogen, phosphorus, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodine, a carbon-containing gas, and mixtures thereof.

10. The method as defined in claim 1, wherein said working gas is selected from the group consisting of nitrogen, hydrogen, noble gases and mixtures thereof.

11. The method as defined in claim 1, wherein said vapor species are cooled in step (D) to become nanometer-sized powder particles and step (D) is followed by a step (F) which comprises operating a powder collector for collecting said powder particles.

12. The method as defined in claim 3, wherein said step (D) includes a sub-step of operating means for injecting a cooling gas into said vapor species, thereby minimizing agglomeration of said nanometer-sized powder material.

13. The method as defined in claim 1, wherein said working gas flow direction is arranged to be approximately vertically downward.

14. The method as defined in claim 1, wherein said at least a starting material comprises two different materials.

15. The method as defined in claim 14, wherein said two different materials make up the two wires in such a manner that the two wires have different material compositions.

16. The method as defined in claim 14, wherein said two different materials include indium and tin.

17. The method as defined in claim 14, wherein said two different materials include antimony and tin.

18. The method as defined in claim 1, further including a step of positioning a reservoir at the bottom portion of said twin-wire arc or a distance below said twin-wire arc in such a fashion that said reservoir receives said stream of liquid droplets from the wires and exposes said liquid to said second energy source to vaporize at least a portion of said liquid.

19. The method of claim 1, wherein said step (D) includes a sub-step of passivating said vapor species to stabilize said nano-structured material.

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