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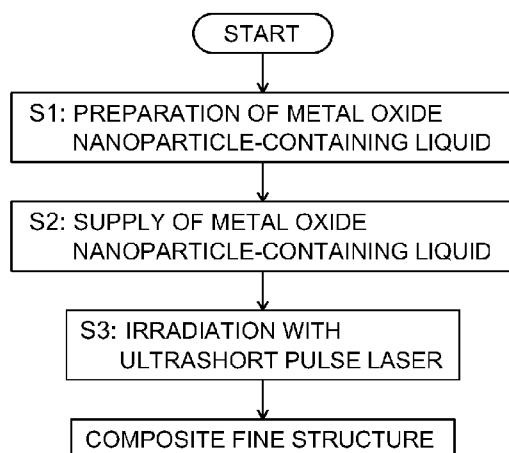
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(54) Title: COMPOSITE FINE STRUCTURE AND METHOD FOR PRODUCING SAME

[Fig. 1]



(57) Abstract: Provided is a novel technique for producing a composite fine structure, which is constituted from a micron sized metal portion and a micron sized metal oxide portion containing an oxide of the metal, by using a direct writing technique. Provided by this technique is a method for producing a composite fine structure that contains a metal portion and a portion of an oxide of the metal. This production method includes preparing a metal oxide nanoparticle-containing liquid, which contains metal oxide nanoparticles and a laser-curable resin that is cured by being irradiated with laser light, and irradiating these metal oxide nanoparticles with an ultrashort pulse laser. A composite fine structure is formed by the irradiation with the ultrashort pulse laser, the composite fine structure containing: a metal oxide portion containing a resin portion in which the laser-curable resin is cured, and the metal oxide nanoparticles; and a metal portion in which the metal oxide nanoparticles are reduced and bonded to each other, the dimension of at least one of the metal oxide portion and the metal portion being 100 μm or less.



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Description

Title of Invention: COMPOSITE FINE STRUCTURE AND METHOD FOR PRODUCING SAME

Technical Field

[0001] The present invention relates to a composite fine structure constituted from a micron sized metal portion and a micron sized metal oxide portion, and a method for producing same.

The present application claims priority on the basis of Japanese Patent Application No. 2015-058170, which was filed on 20 March 2015 and Japanese Patent Application No. 2015-230045, which was filed on 25 November 2015, and the entire contents of that application are incorporated by reference in the present specification.

Background Art

[0002] As electronic elements and semiconductor elements have increased in terms of performance, speed and integration, attention has been focused on techniques for forming fine structures such as small mechanical components and micro electro mechanical systems (MEMS). Because direct writing techniques such as laser lamination shaping methods, fused deposition modeling methods, and ink jet methods enable simplification of processes, unlike lithography techniques that involve the use of masks, development of techniques for producing fine structures by means of these direct writing techniques has progressed in recent years. However, most of these direct writing techniques involve writing on photosensitive resin materials, and techniques for producing fine structures formed of metal materials are still at the research stage.

Citation List

Patent Literature

[0003] [PTL 1] Japanese Patent Application Publication No. 2013-247181

Non-Patent Literature

[0004] [NPL 1] J. Phys. Chem. C 2011, 115, 23664-23670

[NPL 2] ACS Nano, 2014, 8(10), pp 9807-9814

Summary of Invention

Technical Problem

[0005] For example, Patent Document 1 discloses a method for producing a sintered body formed of a metal nanoparticle sintered body by coating a base material with a paste containing metal nanoparticles so as to form a coating film, and irradiating this coating film with laser light. However, this method is not able to avoid overheating of the base material by the laser in an air atmosphere, and has the drawback of requiring

processing to be carried out in, for example, an inert atmosphere.

In addition, Non-Patent Documents 1 and 2 each disclose a method for producing a fine metal electrode by coating a base material with a paste containing nanoparticles of a metal oxide so as to form a coating film and then irradiating this coating film with laser light so as to reduce the metal oxide. In these methods, however, it is not possible to control re-oxidation, which occurs at the same time as the metal oxide nanoparticles are reduced and sintered. Therefore, it was difficult to produce, for example, a micron sized low resistance metal fine structure with good precision.

[0006] Therefore, it is the case that techniques for producing fine structures formed of metal materials by means of direct writing techniques have not yet reached the practical application stage, and establishment of direct writing techniques is required. With these circumstances in mind, an objective of the present invention is to provide a micron sized composite fine structure, which is constituted from a metal oxide portion and a metal portion obtained by reducing the metal oxide, by means of a direct writing technique. In addition, an objective of another aspect of the invention is to provide a novel technique for producing this micron sized composite fine structure.

Solution to Problem

[0007] The technique disclosed here provides a method for producing a composite fine structure containing a metal portion and an oxide portion. This production method includes: preparing a nanoparticle-containing liquid, which contains metal oxide nanoparticles and a laser-curable resin that is cured by being irradiated with laser light; supplying the metal oxide nanoparticle-containing liquid to the surface of a base material; and irradiating the metal oxide nanoparticle-containing liquid supplied to the surface of the base material, with an ultrashort pulse laser. In addition, this production method is characterized in that a micron sized composite fine structure is formed by the irradiation with the ultrashort pulse laser, the composite fine structure containing: a metal oxide portion containing a resin portion in which the laser-curable resin is cured, and the metal oxide nanoparticles; and a metal portion in which the metal oxide nanoparticles are reduced and bonded to each other, the dimension of at least one of the metal oxide portion and the metal portion being 100 μm or less.

[0008] By using an ultrashort pulse laser in the technique disclosed here, thermal effects during the reduction of the metal oxide nanoparticles are substantially controlled and the metal oxide portion that contains the metal oxide nanoparticles can be formed separately from the metal portion in which these metal oxide nanoparticles are reduced. In this way, a composite fine structure which is constituted from a combination of a metal portion and a metal oxide portion and which can exhibit a wide variety of compositions, structures and physical properties can be produced in a simple

manner by using, for example, a single material and a single ultrashort pulse laser oscillator.

[0009] In the present specification, the term "ultrashort pulse laser" means a pulse laser having a pulse duration of less than a nanosecond (10^{-9} s), and can typically be a pulse laser having a pulse duration of several hundred picoseconds (10^{-10} s) or less, and typically 10^{-12} s or less, for example 10^{-14} s or less. This ultrashort pulse laser can include so-called picosecond lasers, femtosecond lasers, attosecond lasers, and the like.

[0010] Moreover, these ultrashort pulse lasers generally have pulse durations that are shorter than heat transfer durations. That is, the pulse duration of an ultrashort pulse laser is shorter than the time required for heat to diffuse to an adjacent atom through a crystal lattice. Therefore, it has been predicted that most of the energy imparted by the laser is absorbed by atoms without being diffused, and does not contribute to reactions. The technique disclosed here can enable precise formation of a composite fine structure by using this type of pulse laser.

[0011] In addition, the term "laser-curable resin" generally encompasses, in a broad sense, polymeric organic compounds that are cured by being irradiated with laser light. Here, polymeric organic compounds being cured may be polymers in which a curing reaction (typically crosslinking or polymerization) progresses upon irradiation with laser light (photosensitive polymers) or polymers that are cured by heat generated as a result of thermal energy converted from laser light energy.

[0012] A preferred aspect of the method for producing a composite fine structure disclosed here is characterized by the metal oxide nanoparticles containing at least one type of oxide selected from the group consisting of oxides of gold (Au), silver (Ag), copper (Cu), nickel (Ni), iron (Fe) and titanium (Ti). In this way, a composite fine structure that exhibits a variety of chemical, physical, mechanical electrical and magnetic characteristics can be produced in a simple manner.

[0013] A preferred aspect of the method for producing a composite fine structure disclosed here is characterized in that the laser-curable resin contains polyvinylpyrrolidone. In this way, the metal oxide portion can exhibit an arbitrary shape in which metal oxide nanoparticles are fixed by these laser-curable resins.

[0014] A preferred aspect of the method for producing a composite fine structure disclosed here is characterized in that the nanoparticle-containing liquid further contains a reducing agent. Here, the reducing agent preferably contains at least one type of reducing agent selected from the group consisting of ethylene glycol, poly(ethylene glycol), formic acid, hydrogen peroxide and toluene. In this way, the composite fine structure can be produced efficiently.

[0015] A preferred aspect of the method for producing a composite fine structure disclosed here is characterized in that the nanoparticle-containing liquid further contains a

dispersing agent. Here, the dispersing agent is preferably one containing at least either of polyvinylpyrrolidone and a silicone resin. In this way, it is possible to produce a composite fine structure which is more compact and which has few variations in terms of structure.

- [0016] A preferred aspect of the method for producing a composite fine structure disclosed here is characterized in that at least some of the metal oxide nanoparticles contained in the metal oxide portion have a core-shell type structure obtained by the surface of metal nanoparticles being oxidized. In this way, it is possible to produce composite fine structures having a variety of constitutions, such as constitutions in which physical properties derived from the metal oxide portion are suppressed.
- [0017] Another aspect of the technique disclosed here provides a composite fine structure. This composite fine structure is characterized by containing a metal oxide portion containing metal oxide nanoparticles, and a metal portion in which the metal oxide nanoparticles are reduced and bonded to each other, and characterized in that the dimension of at least one of the metal oxide portion and the metal portion is 100 μm or less. In this way, a micron sized composite fine structure which contains a metal portion and metal oxide portion, which exhibit different characteristics from each other, is provided.
- [0018] In the composite fine structure disclosed here, it is preferable for the metal portion to be constituted by at least some of the metal oxide nanoparticles being reduced and directly bonded to each other. In addition, the metal oxide portion and metal portion are integrated with each other.
- In addition, it is preferable for the metal oxide nanoparticles to contain oxides of at least one type of metal element selected from the group consisting of gold (Au), silver (Ag), copper (Cu), nickel (Ni), iron (Fe) and titanium (Ti).
- [0019] A preferred aspect of the composite fine structure disclosed here is characterized in that the metal oxide portion further contains a laser-curable resin and at least some of the metal oxide nanoparticles are bonded to each other by means of the laser-curable resin. In this way, it is possible to impart the metal oxide portion with a wider variety of characteristics. This metal oxide portion is known as a first metal oxide portion.
- [0020] A preferred aspect of the composite fine structure disclosed here is characterized in that at least some of the metal oxide nanoparticles in the metal oxide portion are directly bonded to each other. In this way, it is possible to increase the mechanical strength of the metal portion. This metal oxide portion is formed by re-oxidation of the metal portion, and the laser-curable resin is lost. This metal oxide portion is known as a second metal oxide portion.
- [0021] In a preferred aspect of the composite fine structure disclosed here, the first metal oxide portion accounts for 50 vol.% or more of a total volume of the first metal oxide

portion and the second metal oxide portion. In this way, re-oxidation of the metal portion is suppressed and a composite fine structure in which the metal portion and the metal oxide portion are clearly separated is realized.

[0022] A preferred aspect of the composite fine structure disclosed here is characterized in that at least some of the metal oxide nanoparticles contained in the metal oxide portion have a core-shell type structure obtained by oxidizing the surface of metal nanoparticles obtained by reducing the metal oxide nanoparticles. In this way, the metal oxide portion can have a wider variety of constitutions.

[0023] In the composite fine structure described above, a variety of elements can be considered as the metal elements that constitute the metal portion and metal oxide portion. Therefore, composite fine structures having a variety of physical properties can be realized. Preferred examples of articles that contain such composite fine structures include microturbine components, micro-wiring and temperature sensors.

Brief Description of Drawings

[0024] [fig.1]FIG. 1 is a flow chart for a method for producing a composite fine structure according to one embodiment.

[fig.2]FIG. 2 is a diagram that explains the formation of a metal portion (A) and a metal oxide portion (B) in a method for producing a composite fine structure according to one embodiment.

[fig.3]FIG. 3 is an example of Ellingham diagram for metal oxides.

[fig.4]FIG. 4 (a) is a CAD drawing of a microturbine main body according to one embodiment, and FIG. 4 (b) is an optical microscope image of a microturbine main body according to one embodiment.

[fig.5A]FIG. 5A is a perspective view (a) and a layered cross-sectional view (b) of a micro-wire according to one embodiment.

[fig.5B]FIG. 5B is an optical microscope image of a micro-wire according to one embodiment.

[fig.5C]FIG. 5C is an optical microscope image of a micro-wire according to another embodiment.

[fig.6]FIG. 6 is a drawn pattern (a) and an optical microscope image (b) of a composite fine structure according to one embodiment.

[fig.7]FIG. 7 is a diagram that shows the relationship between the pulse energy of an ultrashort pulse laser and the line width in a composite fine structure when producing a composite fine structure according to one embodiment.

[fig.8]FIG. 8 is a diagram that shows the relationship between the pulse energy of an ultrashort pulse laser and the line width in a composite fine structure when producing a composite fine structure according to another embodiment.

[fig.9]FIG. 9 (a) and (b) are optical microscope images of composite fine structures produced under different laser conditions.

[fig.10]FIG. 10 is a diagram that shows the relationship between line width and electrical resistance in a composite fine structure according to one embodiment.

[fig.11]FIG. 11 is a diagram that shows the relationship between the scanning speed of an ultrashort pulse laser and the Ni/NiO ratio when producing a composite fine structure according to one embodiment.

[fig.12]FIG. 12 is a diagram that shows the relationship between the scanning speed of an ultrashort pulse laser and the line width in a composite fine structure when producing a composite fine structure according to one embodiment.

[fig.13]FIG. 13 (a) and (b) are diagrams that explain the formation of drawn patterns in a composite fine structure according to one embodiment.

[fig.14]FIG. 14 is a diagram that explains the constitution of a fine element (a) according to one embodiment and an SEM image of a composite fine structure (b).

[fig.15]FIG. 15 are diagrams that show the resistance-temperature characteristics of composite fine structures having a Cu-rich composition (a) and a Cu₂O-rich composition (b) according to one embodiment.

[fig.16]FIG. 16 is a schematic view that shows the constitution a three-dimensional device according to one embodiment.

Description of Embodiments

[0025] While explaining the method for producing a composite fine structure of the present invention, an explanation will also be given of a composite fine structure provided by the present invention. Moreover, matters which are essential for carrying out the invention and which are matters other than those explicitly mentioned in this specification (ordinary technical matters such as raw materials and devices used when producing the composite fine structure) are matters that a person skilled in the art could understand to be matters of design on the basis of the prior art in this technical field. The present invention can be carried out on the basis of the matters disclosed in the present specification and drawings and common technical knowledge in this technical field. In addition, in the present specification, numerical ranges indicated by "A to B" mean not lower than A and not higher than B.

[0026] FIG. 1 is a flow chart for a method for producing the composite fine structure disclosed here. The composite fine structure will be explained in detail later, but is a structure that contains a metal portion (A) and a metal oxide portion (B). This production method substantially includes steps (S1) to (S3) below. The various steps will now be explained.

(S1) Preparation of metal oxide nanoparticle-containing liquid.

(S2) Supply of metal oxide nanoparticle-containing liquid.

(S3) Irradiation with ultrashort pulse laser.

[0027] <S1. Preparation of metal oxide nanoparticle-containing liquid>

First, a metal oxide nanoparticle-containing liquid, which is used in the production of the composite fine structure, is prepared in step S1. This metal oxide nanoparticle-containing liquid contains metal oxide nanoparticles, which are one part of a material that constitutes the composite fine structure, and a laser-curable resin in an uncured state. In cases where the laser-curable resin is a liquid, it is possible to use the laser-curable resin as a dispersion medium for the metal oxide nanoparticles. In cases where the laser-curable resin is not in a suitable liquid state or is not in a state that is suitable for the subsequent supply step, it is possible to incorporate, in addition to the metal oxide nanoparticles and laser-curable resin, a dispersion medium able to appropriately disperse the metal oxide nanoparticles and laser-curable resin.

[0028] The metal oxide nanoparticles are contained in the metal oxide portion in the composite fine structure. In addition, the metal element that constitutes the metal oxide also constitutes the metal portion. These metal oxide nanoparticles can be nanoparticles that contain the metal oxide in at least a part thereof. In addition, the metal portion of the composite fine structure is a metal formed of the metal element that constitutes the metal oxide nanoparticles, and typically contains a metal obtained by reducing the metal oxide nanoparticles. Therefore, a metal element is present mainly in the metal oxide portion and the metal portion. From this perspective, the composition of the metal oxide nanoparticles is important in order to obtain a composite fine structure that exhibits the desired characteristics. The metal element that constitutes the metal oxide nanoparticles is not particularly limited, and a variety of metal elements can be considered. Specifically, it is possible to consider, for example, a metalloid element such as beryllium (B), silicon (Si), germanium (Ge), antimony (Sb) or bismuth (Bi); a typical element such as manganese (Mg), calcium (Ca), strontium (Sr), barium (Ba), zinc (Zn), aluminum (Al), gadolinium (Gd), indium (In), tin (Sn) or lead (Pb); or a transition metal element such as scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), silver (Ag) or gold (Au).

[0029] Moreover, in the Ellingham diagram shown in FIG. 3, for example, the metal oxides shown at the top of the diagram (which have higher standard formation free energies) are preferred materials due to being able to be reduced relatively easily. In addition, the metal oxides shown at the bottom of the Ellingham diagram (which have lower standard formation free energies) can be preferred materials due to being stable as oxides and being able to stabilize the shape precision of the composite fine structure.

Here, the inventors of the present invention confirmed that the composite fine structure disclosed here can be produced using, for example, metal oxide nanoparticles that fall within the range between AgO and TiO₂ in the Ellingham diagram. In addition, reduction and re-oxidation of the metal oxide nanoparticles can be controlled to a high degree in the present invention. Therefore, a desired metal element can be selected as the metal element that constitutes the metal oxide nanoparticles on the basis of the characteristics inherent in the metal element.

[0030] For example, of the metal elements listed above, Au, Ag, Cu, Ni, Fe, titanium (Ti), and the like, which are in demand for use in MEMS and the like, are preferred as this metal element. For example, in applications in which micro-wires used as conducting wires and the like are formed, Au, Ag or Cu, or the like, which exhibit good electrical conductivity, should be selected as the metal element and metal oxide nanoparticles made of oxides of these metals (that is, Au₂O₃, Ag₂O₃, AgO, Ag₂O, CuO, Cu₂O, or the like) should be prepared. Alternatively, metal oxide nanoparticles which contain, at least in a part thereof, oxides of these metals (that is, Au₂O₃, Ag₂O₃, AgO, Ag₂O, CuO or Cu₂O) should be prepared. It is possible for one of these metal elements to constitute the metal oxide in isolation or for two or more of these metal elements to constitute the metal oxide in combination.

[0031] In addition, the metal oxide nanoparticles may be constituted entirely or partially from the metal oxide. For example, the metal oxide nanoparticles may be nanoparticles that contain the metal oxide in all or a part thereof. For example, the metal oxide nanoparticles may be nanoparticles that contain the metal oxide on all or at least a part of the surface thereof. In such cases, the metal oxide nanoparticles may be core-shell type particles having a core-shell type structure. Metal oxide nanoparticles having a core-shell type structure preferably contain the metal oxide as the shell portion. The material that constitutes the core portion of the core-shell type particles is not particularly limited. For example, the material that constitutes the core portion may be the metal oxide mentioned above, a metal oxide other than this, a variety of metals, a ceramic, a glass, an organic polymer material, or the like. The shape of the metal oxide nanoparticles is not particularly limited, and may be a variety of shapes, such as spherical, rod-shaped, plate-shaped or monolithic.

[0032] The average particle diameter of the metal oxide nanoparticles is not particularly limited, and can be, for example, approximately 100 nm or lower. However, in order to make the composite fine structure more compact and dimensionally precise, it is preferable for the average particle diameter of the metal oxide nanoparticles to be lower. For example, the average particle diameter is preferably 50 nm or lower, more preferably 20 nm or lower, and particularly preferably 10 nm or lower (for example, approximately 2 to 5 nm).

Moreover, the average particle diameter of the metal oxide nanoparticles can be a value measured using dynamic light scattering (DLS). For example, it is possible to use a particle diameter corresponding to a cumulative 50% in a particle size distribution based on frequency analysis of scattered light (the median diameter D_{50}).

[0033] In addition, the metal oxide nanoparticles may be ones obtained through preparation from raw materials or metal oxide nanoparticles that are commercially available in the form of, for example, a dispersion liquid or the like. From this perspective also, the metal oxide nanoparticle-containing liquid may contain a dispersion medium able to advantageously disperse the metal oxide nanoparticles. The dispersion medium is not particularly limited, and typical examples thereof include a variety of hydrocarbons; halogenated hydrocarbons; alcohols such as methanol, ethanol, butanol, isobutanol and isopropanol; glycols such as poly(ethylene glycol); phenol compounds; ethers; ketones such as acetone and methyl ethyl ketone; acetals such as polyacetals; esters; amines such as n-butylamine; unsaturated fatty acids; and types of water such as ion exchanged water, distilled water and pure water.

[0034] The laser-curable resin can be a variety of resins able to be cured by being irradiated with laser light, as mentioned above. For example, it is possible to use a photosensitive resin able to be cured by irradiated laser light having a prescribed wavelength initiating a polymerization reaction or a thermosetting resin able to be cured by heat generated by laser light irradiation initiating a polymerization reaction. These laser-curable resins may contain a suitable polymerization initiator if necessary.

[0035] Photosensitive resins encompass a wide variety of resin materials that are cured when crosslinking or polymerization is initiated as a result of absorption of light generated by laser light irradiation. This type of photosensitive resin may be a resin obtained when polymerization of a polymerizable monomer is initiated by absorption of direct light or a sensitized photopolymerization type resin obtained when polymerization of a sensitizer-containing polymerizable monomer is initiated by absorption of light having a wavelength other than the absorption wavelength region. It is publicly known by persons skilled in the art that innumerable such photosensitive resins are known, but examples thereof include direct photopolymerization type resins represented by resins of vinyl chloride, styrene, methyl methacrylate and derivatives thereof; and sensitized photopolymerization type resins represented by resins of ethylene, vinyl chloride, acetone, butadiene, styrene, triphenylphosphine, methyl methacrylate and derivatives thereof.

[0036] Thermosetting resins encompass a wide variety of resin materials that can be cured when polymerization is initiated by heat derived from heat energy converted from light energy generated by laser light irradiation. Specific examples thereof include phenolic resins (PF), epoxy resins (EP), melamine resins (MF), urea resins (UF), unsaturated

polyester resins (UP), alkyd resins, polyurethanes (PUR) and thermosetting polyimides (PI).

[0037] The laser-curable resins mentioned above can be contained as cured products in the metal oxide portion in the composite fine structure. Therefore, it is possible to select an appropriate thermosetting resin according to the desired characteristics to be imparted to the metal oxide portion. For example, in cases where the metal oxide portion of the composite fine structure requires high insulation properties, it is preferable to use a phenolic resin, such as poly(vinyl phenol), or a thermosetting polyimide or the like as the laser-curable resin. When added to the metal oxide nanoparticle-containing liquid, this laser-curable resin may be in the form of, for example, a mixture of low molecular weight monomers or a polymer in which polymerization has progressed to a certain degree. It is possible to use one of these resins (or monomers) in isolation, or a combination (including a blend) of two or more types thereof.

[0038] In addition, the laser-curable resin may exhibit the function of bonding metal oxide nanoparticles to each other or bonding metal oxide nanoparticles to the base material in the metal oxide portion following irradiation with the ultrashort pulse laser. The proportion of the laser-curable resin in the metal oxide nanoparticle-containing liquid is not particularly limited, but can be, for example, a quantity required to bind the metal oxide nanoparticles. The proportion of this type of laser-curable resin can be 5 to 30 parts by mass, preferably 5 to 25 parts by mass, and more preferably 10 to 20 parts by mass, relative to 100 parts by mass of the metal oxide nanoparticles.

[0039] In addition, the metal oxide nanoparticle-containing liquid may contain additives such as a reducing agent and/or a dispersing agent, but is not necessarily limited to these.

The reducing agent exhibits the function of facilitating a reduction reaction of the metal oxide nanoparticles in the ultrashort pulse laser irradiation step (S3), which is explained later, and can be a variety of compounds able to facilitate this reduction reaction. Specific examples of reducing agents include glycols such as ethylene glycol and poly(ethylene glycol); compounds having aldehyde groups such as aldehydes, formic acid and formic acid esters; hydrogen peroxide; sulfur dioxide; toluene; and polyvinylpyrrolidone. It is possible to use one of these reducing agents in isolation, or a combination of two or more types thereof.

The added quantity of reducing agent is not particularly limited. For example, the added quantity of reducing agent can be, specifically, 1 to 250 parts by mass, preferably 5 to 100 parts by mass, and more preferably 20 to 50 parts by mass, relative to 100 parts by mass of the metal oxide nanoparticles.

[0040] A variety of compounds that exhibit the effect of preventing aggregation of the metal oxide nanoparticles can be used without particular limitation as the dispersing agent.

For example, it is possible to use an anionic, cationic or non-ionic dispersing agent. Specific examples of anionic dispersing agents include polycarboxylic acid type dispersing agents, such as sodium salts of polycarboxylic acids and ammonium salts of polycarboxylic acids, naphthalene sulfonic acid type dispersing agents, such as sodium salts of naphthalene sulfonic acid and ammonium salts of naphthalene sulfonic acid, alkylsulfonic acid type dispersing agents, and polyphosphoric acid type dispersing agents. Examples of cationic dispersing agents include polyalkylene polyamine type dispersing agents, quaternary ammonium type dispersing agents and alkylpolyamine type dispersing agents. Examples of non-ionic dispersing agents include alkylene oxide type dispersing agents, polyhydric alcohol ester type dispersing agents, dispersing agents based on N-vinyl lactam compounds, such as polyvinylpyrrolidone, and silicone resin type dispersing agents, such as cyclopentasiloxane and dimethylpolysiloxane. It is possible to use one of these dispersing agents in isolation, or a combination of two or more types thereof.

[0041] The added quantity of dispersing agent is not particularly limited, and can be determined according to, for example, the average particle diameter or surface condition of the metal oxide nanoparticles being used. For example, the added quantity of dispersing agent can be specifically 1 to 30 parts by mass, preferably 1 to 25 parts by mass, and more preferably 1 to 20 parts by mass, relative to 100 parts by mass of the metal oxide nanoparticles.

[0042] Moreover, the metal oxide nanoparticle-containing liquid may contain additives other than the reducing agents and dispersing agents mentioned above as long as the objective of the present invention is not impaired. One example of such an additive is a viscosity modifier. By adjusting the viscosity of the metal oxide nanoparticle-containing liquid as appropriate, it is possible to increase the dispersibility of the metal oxide nanoparticles and supply the metal oxide nanoparticle-containing liquid to a base material in an advantageous manner in a subsequent step. The viscosity modifier is not particularly limited, but examples thereof include non-ionic polymers, for example a polyether such as poly(ethylene glycol).

With regard to these reducing agents, dispersing agents and other additives, the same compound can function as two or more additives.

[0043] It is possible to prepare the metal oxide nanoparticle-containing liquid by homogeneously mixing the materials mentioned above. The proportion (concentration) of the metal oxide nanoparticles in the overall metal oxide nanoparticle-containing liquid is not particularly limited, but should be adjusted to be, for example, 5 to 80 mass %, preferably 10 to 80 mass %, and particularly preferably 30 to 60 mass %. These materials can be mixed using a variety of publicly known apparatuses used for stirring, mixing or emulsifying, such as a mixer, an ultrasonic stirring device, a shear stirring

device or a homogenizer. The order in which the materials mentioned above are stirred is not particularly limited, and it is possible to, for example, mix all of the materials together or divide the materials into a plurality batches and mix separately. For example, in a system in which a dispersion medium is used, it is possible to introduce the metal oxide nanoparticles and a dispersing agent into the dispersion medium, stir, and then add the laser-curable resin, the reducing agent, and the like.

[0044] <S2. Supply of metal oxide nanoparticle-containing liquid>

In step S2, the metal oxide nanoparticle-containing liquid prepared in the manner described above is supplied to a surface of a base material. The material and shape of the base material are not limited. For example, it is possible to use a base material formed of a semiconductor material, an inorganic material such as a ceramic, an amorphous material such as a glass, a metal material, a resin material, or the like. In addition, the surface of the base material may be a smooth surface, a curved surface or a surface provided with protrusions and recesses. Furthermore, the base material may be able to be deformed into a curve or the like (a flexible base material), but may also have a fixed shape. In addition, the base material may be a material that is able to be separated from the composite fine structure following production, or a material able to be removed from the composite fine structure following production. For example, the base material may be subjected to a treatment (separation facilitation treatment) so as to enable separation of the base material from the composite fine structure following production.

[0045] The means for supplying the metal oxide nanoparticle-containing liquid to the base material is not particularly limited. For example, it is possible to use a variety of publicly known methods, such as coating methods, screen printing methods, casting methods, dip coating methods, spin coating methods, electrophoresis methods, spraying methods and ink jet methods. By doing so, it is possible to form a layered product formed of the metal oxide nanoparticle-containing liquid on the base material.

Moreover, the supply of the metal oxide nanoparticle-containing liquid is not limited to a single supply, and the supply may be carried out a plurality of times. That is, it is possible to set the number of times the metal oxide nanoparticle-containing liquid is supplied to be one time or a plurality of times in order to, for example, supply (coat) the metal oxide nanoparticle-containing liquid at a desired thickness. In addition, it is possible to alternately repeat the subsequent ultrashort pulse laser irradiation step (S3) and the metal oxide nanoparticle-containing liquid supply step (S2) a plurality of times. For example, by repeatedly supplying the metal oxide nanoparticle-containing liquid and irradiating with an ultrashort pulse laser, it is possible to form a composite fine structure having a complex three-dimensional structure.

[0046] <S3. Irradiation with ultrashort pulse laser>

In step S3, the metal oxide nanoparticle-containing liquid supplied to the surface of the base material is irradiated with an ultrashort pulse laser. The ultrashort pulse laser can carry out irradiation by using a variety of laser oscillators able to oscillate a pulse laser having a pulse duration of less than a nanosecond (10^{-9} s). For example, laser irradiation can be conveniently carried out by using a commercially available ultrashort pulse laser writing apparatus. Moreover, the ultrashort pulse laser can be irradiated in an air atmosphere.

In the technique disclosed here, by adjusting the conditions under which the ultrashort pulse laser irradiates the metal oxide nanoparticle-containing liquid supplied to the base material, as shown in FIG. 2, the metal portion (A) and the metal oxide portion (B) are formed as portions having different constitutions. In addition to the metal portion (A) and the metal oxide portion (B), unreacted portions (C) of the metal oxide nanoparticle-containing liquid are present in the metal oxide nanoparticle-containing liquid following irradiation with the ultrashort pulse laser. Here, the unreacted portions (C) are portions where the metal oxide nanoparticle-containing liquid has been supplied but the laser-curable resin has not been cured. By removing these unreacted portions (C) by, for example, rinsing with a suitable solvent, it is possible to obtain a composite fine structure formed of the metal portion (A) and the metal oxide portion (B). The solvent used for this washing can be, for example, a dispersion medium or the like able to be used in the metal oxide nanoparticle-containing liquid. Alternatively, it is possible to produce a composite fine structure by irradiating with an ultrashort pulse laser under conditions whereby at least the laser-curable resin is cured throughout the metal oxide nanoparticle-containing liquid, so that unreacted portions (C) are not formed. A composite fine structure obtained in this way can be one in which the metal portion (A) and the metal oxide portion (B) are formed at micron sizes with extremely fine precision.

[0047] Here, the metal oxide portion (B) is a portion that contains metal oxide nanoparticles. More typically, the metal oxide portion (B) contains a resin portion in which the laser-curable resin contained in the metal oxide nanoparticle-containing liquid is cured, and metal oxide nanoparticles. Specifically, the laser-curable resin becomes a resin portion by being cured when irradiated with an ultrashort pulse laser, binds adjacent metal oxide nanoparticles to each other and binds metal oxide nanoparticles to the base material. Therefore, for example, by irradiating with an ultrashort pulse laser under conditions whereby the laser-curable resin can be cured in a prescribed region, it is possible to form a metal oxide portion having a shape corresponding to the irradiated region. The metal oxide portion (B) can exhibit physical properties derived mainly from the metal oxide, although this depends on the proportion of the metal oxide.

[0048] In addition, the metal portion (A) is a portion in which metal nanoparticles are

formed by metal oxide nanoparticles being reduced, and is constituted by these metal nanoparticles being bound to each other. The reduction and binding of the metal oxide nanoparticles may progress simultaneously, but it is also possible for one of these to occur first. Moreover, under laser irradiation conditions whereby reduction of metal oxide nanoparticles occurs, the resin portion seen in the metal oxide portion (B) can be decomposed and lost. Therefore, it can be thought that this metal portion (A) contains substantially no organic compounds, such as the laser-curable resin or other additives. This metal portion (A) can exhibit physical properties derived substantially from the metal.

[0049] Moreover, the metal portion (A) is typically formed by metallized nanoparticles binding to each other after reduction of the metal oxide nanoparticles starts. The reduction of the metal oxide nanoparticles can be achieved by reducing all or some of the metal oxide contained in the metal oxide nanoparticles. In other words, all or some of the metal oxide contained in the metal oxide nanoparticles may be metallized to the elemental metal that constitutes the metal oxide. In addition, the metal portion (A) is formed by at least some of the sites formed of metallized metal in the metal oxide nanoparticles (hereinafter referred to simply as "metallized sites") directly binding to each other. Therefore, the metal portion (A) may be constituted only from the metal that constituted the metal oxide, but may also contain unreduced metal oxide or products formed by modification of the metal oxide. For example, in cases where the metal oxide nanoparticles formed entirely of the metal oxide, when the entire metal oxide is reduced, the metal portion (A) is formed as a bound material of metal nanoparticles formed of the metal that constituted the metal oxide.

[0050] The metal portion (A) is formed by the metal oxide nanoparticles being reduced when irradiated with a laser, and the laser-scanned surface therefore has at least metallized sites. The laser-scanned surface can typically be an exposed surface, but in cases where the composite fine structure has a three-dimensionally formed shape, the laser-scanned surface can be contained within the structure. In addition, because at least some of the metallized sites (A) are metallized, a so-called metallic luster can be observed. A metallic luster can even be observed in cases where metallized sites (A) include unreduced metal oxide. Therefore, when the entire composite fine structure is observed, the metal oxide portion (B) can be distinguished from the metal oxide portion (B) in an unreduced state because a metallic luster can be observed at the metallized sites (A). For example, the metallized sites (A) can be ascertained as sites having higher light reflectance than the metal oxide portion (B).

[0051] In the metal portion (A), it is preferable for metallized sites to account for 10 mass % or more of the total mass of sites formed of the metal oxide and metallized sites formed of the metal that constitutes the oxide, although this proportion varies according to the

type of metal that constitutes the metal oxide and the form of the metal oxide nanoparticles, and cannot therefore be generalized. The proportion of metallized sites in the metal portion (A) is preferably 30 mass % or higher, and more preferably 40 mass % or higher, for example 50 mass % or higher.

- [0052] In the reduced metal oxide nanoparticles in the metal portion (A), at least a part of the particle surface can be melted and then solidified, thereby binding adjacent metal nanoparticles to each other. It is possible for some or all of the reduced metal oxide nanoparticles to be melted. Alternatively, adjacent reduced metal oxide nanoparticles may be bound to each other through sintering without being melted. Moreover, in cases where the surface of metal oxide nanoparticles melts, the metal portion (A) can be strongly bound to the base material also.
- [0053] Moreover, the composite fine structure disclosed here the metal oxide portion (B) may contain (B') a portion that contains a metal oxide while containing substantially no resin portion (referred to as the second metal oxide portion for the sake of convenience), but is not necessarily limited to such cases. That is, it can be thought that the resin portion, which is seen in the metal oxide portion (B), is lost from this second metal oxide portion (B') as a result of irradiation with the ultrashort pulse laser. Here, the second metal oxide portion (B') is not present in the metal oxide nanoparticles used as a raw material (the unreacted metal oxide nanoparticles), and can typically be formed by the metal portion (A) being re-oxidized. That is, metal oxide nanoparticles are directly bound to each other in this second metal oxide portion (B'), despite this being a metal oxide portion (B). Alternatively, while the metal oxide nanoparticles are melted and integrated with each other, at least the laser-scanned surface (which may be an exposed surface or the like) of these metal oxide nanoparticles is constituted from the metal oxide. This type of second metal oxide portion (B') may be in a form whereby all of the metal portion (A) is re-oxidized. Moreover, a mode in which only some of the metal portion (A) is re-oxidized can be regarded as metal portion (A).
- [0054] As explained later, the technique disclosed here enables the production of a composite fine body in which re-oxidation of the metal portion (A) can be advantageously suppressed. Therefore, it is possible to make the proportion of the first metal oxide portion relative to the overall volume of the first metal oxide portion and a second metal oxide portion in the composite fine structure 50 vol.% or higher, more preferably 60 vol.% or higher, and particularly preferably 70 vol.% or higher. If re-oxidation progresses, the metal portion completely melts and foams, and it is difficult to achieve a fine processing effect using an ultrashort pulse laser. From this perspective, it is preferable for the proportion of the first metal oxide portion to be high. In other words, it is preferable for the proportion of the second metal oxide portion to be low.

[0055] Moreover, in cases where the metal element in the prepared metal oxide nanoparticles constitutes an oxide at a divalent or higher valency, it is possible to form an oxide having a different valency that falls between the valency of the metal oxide and that of the metal (zero valency) (hereinafter referred to as a lower metal oxide). That is, a new lower metal oxide can be formed by the original metal oxide being reduced. This lower metal oxide may be contained in the metal portion (A) or in the metal oxide portion (B). The composite fine structure disclosed here is not necessarily limited to this, but a metal oxide portion (B'') formed of a lower metal oxide that is different from the original metal oxide (hereinafter referred to as a third metal oxide portion for the sake of convenience) can be contained in the metal oxide portion (B). This third metal oxide portion (B'') can exhibit physical properties derived substantially from this lower metal oxide.

[0056] In the composite fine structure described above, the metal portion (A) and metal oxide portions (B) to (B'') may be disposed arbitrarily in the composite fine structure, and the metal portion (A) and metal oxide portions (B) to (B'') may be contained singly or multiply in a single composite fine structure.

In addition, because the degree of reduction of the metal oxide nanoparticles can be controlled precisely according to the technique disclosed here, separate explanations have been given for the metal oxide portion (B), the second metal oxide portion (B') and the third metal oxide portion (B''). However, the metal oxide portion (B) and the second metal oxide portion (B') can both exhibit physical properties derived from the same metal oxide, and do not therefore necessarily need to be clearly distinguished from each other. For example, the metal oxide portion (B) and the second metal oxide portion (B') should, when necessary, be distinguished from each other depending on the intended use of the composite fine structure, or the like. In addition, the third metal oxide portion (B'') may, or may not, be distinguished from the metal oxide portion (B), depending on the intended use of the composite fine structure, or the like. Explanations will now be given without distinguishing between the metal oxide portions (B) to (B''), unless necessary.

[0057] The metal portion (A) and metal oxide portion (B) described above can be individually formed by, for example, altering some of the irradiation conditions of the ultrashort pulse laser. In other words, even using the same materials and same ultrashort pulse laser writing device, by adjusting the irradiation conditions of the ultrashort pulse laser, which is oscillated by this device, the metal portion (A) and metal oxide portion (B) can be individually formed.

[0058] Moreover, an ultrashort pulse laser is a laser having a pulse duration of less than 1 nanosecond. In metals, metal oxides, and the like, it is said that a period of approximately 1 picosecond is required for heat to diffuse to an adjacent atom through a

(crystal) lattice that constitutes a solid. More specifically, this heat transfer can be estimated from the average free time (also known as the relaxation time or collision relaxation time), which is the average period of time between a conduction electron or the like colliding with another atom and the next collision, and varies according to the target substance and the heating temperature. In addition, it is known that this time is approximately several picoseconds for ordinary metals. Moreover, this average free time can be calculated from, for example, electron-phonon coupling parameters. Therefore, when the laser pulse duration is shorter than the heat transfer, most of the energy imparted by the laser can be absorbed by atoms with diffusing. In addition, during the period between the end of laser irradiation and the next laser irradiation, the lattice is heated by the energy absorbed by the atoms, and then cools. Alternatively, in cases where the absorbed energy is high, the lattice heats and heat conduction can occur.

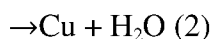
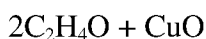
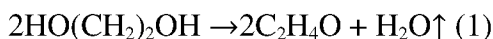
[0059] In the technique disclosed here, by using an ultrashort pulse laser, pulsed energy is supplied for periods that are shorter than the heat transfer time (average free time) in the metal oxide nanoparticles. In addition, the pulsed energy supplied by 1 laser pulse can be precisely controlled. Therefore, the metal oxide nanoparticles can be heated while suppressing thermal diffusion, for example. In this way, by using an ultrashort pulse laser to supply an appropriate quantity of energy according to the composition of the metal oxide that constitutes the nanoparticles, a reaction that forms the metal portion (A) and a reaction for forming the metal oxide portion (B) can be brought about locally and selectively. In addition, portions other than the metal portion (A) and metal oxide portion (B) can remain as unreacted portions (C).

[0060] In order to form the metal oxide portion (B), the ultrashort pulse laser is irradiated under conditions whereby those portions of the laser-curable resin in which the metal oxide portion (B) is to be formed are cured. For example, in cases where the laser-curable resin is a photocurable resin, the laser should be irradiated at a wavelength whereby polymerization of the resin can be initiated. In addition, in cases where the laser-curable resin is, for example, a thermosetting resin, pulsed energy should be supplied to the metal oxide nanoparticles in such a way that the thermosetting resin is heated to a temperature that is not lower than the temperature at which polymerization of the resin can be initiated. Alternatively, pulsed energy should be supplied to metal oxide nanoparticles in such a way that heat transferred to the thermosetting resin from other metal oxide nanoparticles, in which heat has been generated through the supply of pulsed energy, reaches a temperature that is no lower than the temperature at which polymerization of the resin can be initiated. As mentioned above, this pulsed energy quantity can be calculated from the composition and volume of the metal oxide nanoparticles, the temperature of the environment, the physical properties of the ther-

mosetting resin, and the like.

- [0061] In order to form the metal portion (A), metal oxide nanoparticles contained in those parts in which the metal portion (A) is to be formed should be irradiated with the ultrashort pulse laser under conditions whereby the metal oxide can be reduced. The mechanism by which the metal oxide is reduced is not particularly limited. Specifically, for example, the metal oxide nanoparticles should be irradiated with the ultrashort pulse laser under conditions whereby the metal oxide can be heated to a temperature that is not lower than the temperature at which the metal oxide can be reduced. Thermal reduction of the metal oxide can be represented by general formulae (1) and (2) below. In addition, the quantity of energy required for this thermal reduction can be calculated from the composition and volume of the metal oxide nanoparticles, the standard formation free energy thereof, the temperature of the environment, and the like. Metal oxide nanoparticles that have been thermally reduced in this way can be sintered by the increase in temperature of the metal oxide nanoparticles per se. In addition, the laser-curable resin can generally be burned off when heated to a temperature at which thermal reduction can occur. In this way, the metal portion (A) is formed by sintering of reduced metal nanoparticles.

- [0062] (A case in which the metal oxide is CuO, and EG is used as a reducing agent)



- [0063] Moreover, when a quantity of energy greater than that required for the reduction is supplied to the metal oxide nanoparticles, the metal oxide nanoparticles are reduced to metal nanoparticles, and, for example, all or some of the surface of the metal nanoparticles then melts. In such cases, reduced metal nanoparticles melt and then solidify, thereby forming the metal portion (A).

In cases where this type of metal nanoparticle melting occurs, heat conduction can occur from the heated and melted metal nanoparticles to the surroundings. As a result of this heat conduction, the metal oxide nanoparticles are not thermally reduced around the metal portion (A), but regions in which a thermosetting resin is cured can be formed. In this way, the metal oxide portion (B) can be formed.

- [0064] Meanwhile, the metal oxide nanoparticles are not reduced (for example, thermally reduced) in the metal oxide portion (B), but a metal oxide portion (B) can also be formed by heating the metal oxide nanoparticles to a temperature at which the thermosetting resin is cured. The quantity of energy required for this reaction can be calculated from the physical properties of the thermosetting resin being cured (the curing temperature), the composition and volume of the metal oxide nanoparticles, and

the like.

In addition, in cases where the metal oxide nanoparticles can form a lower oxide, the metal oxide nanoparticles are not reduced (for example, thermally reduced) to the metal (which has zero valency), but it is possible to heat the metal oxide nanoparticles in such a way as to be thermally reduced to this lower metal oxide. In this way, it is possible to form a third metal oxide portion (B"). The pulsed energy quantity required to form this third metal oxide portion (B") can be calculated from the compositions, standard formation free energies and volumes of the original metal oxide and lower metal oxide, the temperature of the environment, and the like.

[0065] Meanwhile, a second metal oxide portion (B') can be formed when a quantity of energy that is excessively greater than that required for the reduction is supplied to the metal oxide nanoparticles. That is, the once reduced metal nanoparticles can be readily oxidized by excessive energy, and can again be oxidized to a metal oxide. In this way, the second metal oxide portion (B'), which is obtained through re-oxidation of the metal portion (A), is formed.

Moreover, even in cases where an ultrashort pulse laser is used, if an excessive quantity of energy is supplied, the metal oxide nanoparticles are rapidly heated and melted, which can lead to bumping. When cooled, this bumped portion can be regarded as a second metal oxide portion, but the dimensional precision can be greatly disrupted by the bumping. This type of state is not a preferred mode of the composite fine structure disclosed here. Therefore, supplying an excessive quantity of pulsed energy such that the metal oxide nanoparticles are rapidly heated and melted cannot be said to be desirable.

[0066] Moreover, even if the metal oxide nanoparticle-containing liquid is irradiated with an ultrashort pulse laser, the irradiated region remains unreacted (C) as long as a curing reaction of the laser-curable resin and a reduction reaction of the metal oxide nanoparticles do not occur. That is, because the ultrashort pulse laser has an extremely short pulse duration, a quantity of energy by which a curing reaction or reduction reaction cannot occur is absorbed by the lattice, and is not involved in a reaction due to cooling or the like occurring. Therefore, the irradiation conditions of the ultrashort pulse laser can be adjusted in view of the intensity distribution of the laser oscillated by the ultrashort pulse laser oscillation device being used. In this way, a composite fine structure in which the metal portion (A) and the metal oxide portions (B) to (B") are arbitrarily combined is realized.

[0067] By controlling the irradiation conditions of the ultrashort pulse laser, it is possible to variously adjust the quantity of pulsed energy to be supplied to the metal oxide nanoparticles, as mentioned above. It is difficult to unambiguously specify irradiation conditions for an ultrashort pulse laser so as to advantageously produce a composite

fine structure, but as general guidelines, a preferred example is to set laser oscillation conditions to be a wavelength of 350 to 1560 nm, a pulse duration of 10 fs to 300 ps, a cyclic frequency of 10 kHz to 100 MHz, a maximum pulse energy of 0.2 to 1.2 nJ, a fluence of 1.5 to 15000 J/m², and a scanning speed of 30 to 1500 μm/s.

Moreover, in the embodiments given below, examples of conditions under which the metal portion (A), the metal oxide portions (B) to (B'') and unreacted portions (C) can be formed will be given for the type metal oxide nanoparticles being used. A person skilled in the art could, on the basis of these disclosures, appropriately determine ultrashort pulse laser irradiation conditions under which the metal portion (A), the metal oxide portions (B) to (B'') and unreacted portions (C) can be separately formed.

[0068] Moreover, conditions under which the metal portion (A), the metal oxide portions (B) to (B'') and unreacted portions (C) can be formed do not necessarily need to be determined on the basis of calculations. For example, by actually producing composite fine structures by altering ultrashort pulse laser irradiation conditions and observing the structures of the formed composite fine structures, it is possible to ascertain conditions under which a desired structure can be achieved. For example, this can be simply confirmed by using an electron microscope to investigate the proportions of metal portions and metal oxide portions contained in a composite fine structure. For example, when a plurality of composite fine structures are produced by altering the ultrashort pulse laser irradiation conditions, the proportions of metal portions and metal oxide portions can be investigated using X-Ray diffraction analysis, or the like. In such cases, by mapping the ratio of the intensity (I_M) of a diffraction peak derived from a metal relative to the intensity (I_{MO}) of a diffraction peak derived from a metal oxide (I_{MO}/I_M), for example, it is possible to confirm, for example, ultrashort pulse laser irradiation conditions under which a metal portion can be efficiently formed and ultrashort pulse laser irradiation conditions under which a metal oxide portion can be formed.

[0069] Furthermore, according to detailed investigation by the inventors of the present invention, a linear composite fine structure such as that shown in FIG. 13 (a) is formed by scanning an ultrashort pulse laser in a linear manner (for example, in one direction) under optimal conditions for a metal oxide nanoparticle-containing liquid supplied in the form of a film. This scanning direction is known as "the principal scanning direction". This composite fine structure is constituted by a fixed portion x having a metallic luster (hereinafter referred to as a lustrous portion x) and two fixed non-lustrous portions y (hereinafter referred to as binding portions y) being formed in a linear manner along the principal scanning direction on the inside of unreacted portions z of the metal oxide nanoparticle-containing liquid. In FIG. 13, the scanning line is shown by the dotted and dashed line. The lustrous portion x and binding portions y are

typically formed symmetrically on both sides of the scanning line. In addition, in cases where the laser irradiation conditions are the same, the line widths of the lustrous portion x and binding portions y are approximately uniform.

[0070] Here, the unreacted portions z correspond to the unreacted portions (C) mentioned above. The lustrous portion x is formed as a single band-shaped line centered on the scanning line, is reduced by direct irradiation by the ultrashort pulse laser or by heat generated by the laser, and is thought to be a portion that is melted and then solidified or a portion that is sintered. It is thought that this lustrous portion x corresponds to the metal portion (A) mentioned above. In general, metals have lower sintering temperatures than metal oxides. Therefore, the reduced metal portion (A) is readily sintered. The binding portions y are formed along, and adjacent to, the edges of the metallic lustrous portion x, in such a way that the linear metallic lustrous portion x is sandwiched in a direction that is perpendicular to the scanning direction. It is thought that these binding portions y are portions formed by being bound by resin portions that are cured by conducted heat (heat effects) caused by heat generated by the ultrashort pulse laser. Therefore, it is thought that these binding portions y correspond to the metal oxide portion (B) mentioned above. In addition, the two binding portions y formed at the edges of the metallic lustrous portion x have substantially the same widths.

[0071] Here, as shown in FIG. 13 (b), the scanning line is displaced by a prescribed distance in a secondary scanning direction that is perpendicular to the principal scanning direction, and the ultrashort pulse laser is scanned in the principal scanning direction. Here, the laser irradiation conditions are the same as mentioned above, and the ultrashort pulse laser is scanned in such a way that the lustrous portions x overlap in the first scan and second scan, as shown in (1). Therefore, that portion where the lustrous portions x overlap each other can generally be constituted as a re-oxidized metal oxide portion. That is, formation of a metal portion is suppressed. In addition, if the ultrashort pulse laser is scanned in such a way that the lustrous portion x and a binding portion y overlap, as shown in (2), that portion where the lustrous portion x and the binding portion y overlap each other tend to be constituted from a re-oxidized metal oxide portion. That is, formation of a metal portion is suppressed in this case also. In addition, if the ultrashort pulse laser is scanned in such a way that only the binding portions y overlap in the first and second scans, as shown in (3), that portion where the binding portions y overlap each other tend to be constituted from a reduced metal portion. That is, a metal portion can be advantageously formed in this case. Meanwhile, if the ultrashort pulse laser is scanned in such a way that binding portions y are tightly parallel to each other without overlapping, as shown in (4), composite fine structures such as those shown in FIG. 13 (a) are formed parallel to each other.

Therefore, by setting the pitch of the ultrashort pulse laser in the secondary scanning direction to be (width of lustrous portion x + width of 1 binding portion y), it is possible to scan the ultrashort pulse laser in such a way that only the binding portions y are irradiated twice by the ultrashort pulse laser. In this way, metal portions can be formed in the form of connected surfaces. In view of this characteristic, a composite fine structure having a desired shape can be efficiently formed by investigating the dimensions of the lustrous portion x and binding portions y formed (fixed) by predetermined ultrashort pulse laser irradiation conditions.

[0072] Because diffusion of heat in an irradiation target is suppressed, as mentioned above, the ultrashort pulse laser can form the metal portion (A) and the metal oxide portion (B) with minimal effects from heat diffusion. This dimensional precision can be controlled to the micron level, although this precision depends on the physical properties (composition, particle diameter, and the like) of the metal oxide nanoparticles. For example, a composite fine structure can generally be easily formed while regulating the dimension of at least either a metal oxide portion or a metal portion in the composite fine structure to 100 μm or less. Therefore, in the composite fine structure disclosed here, the dimension of at least either the metal oxide portion or the metal portion can be regulated to 100 μm or less. More preferably, the composite fine structure disclosed here can be formed so that at least one dimension thereof (for example, a line width) is 50 μm or less, preferably 20 μm or less, and particularly preferably 10 μm or less, for example 1 to 8 μm . For example, it is possible to form a sheet having a thickness of approximately 1 to 8 μm even in the case of a planar shape measuring 100 μm x 100 μm or more. It is possible to provide, for example, a hollow portion having an arbitrary shape in the plane of this type of micron -sized sheet-shaped product. For example, by using a publicly known precision laser writing device which can oscillate a femtosecond laser in order to process a photosensitive resin (a laser processing device, three-dimensional laser lamination shaping device, or the like), the composite fine structure disclosed here can be advantageously produced.

[0073] Moreover, in cases where metal oxide portions and metal portions are continuously formed in a composite fine structure, as shown in the embodiments given below, the dimensions of the metal oxide portions and metal portions can exceed 100 μm . Moreover, this term "continuously" is not limited to modes in which, for example, metal oxide portions and/or metal portions having widths of 100 μm or less are formed into a longer length along the laser scanning direction (that is, in one dimension). For example, modes in which metal oxide portions and/or metal portions having widths of 100 μm or less are continuously laminated or bound in a two-dimensional or three-dimensional manner are encompassed. However, the composite fine structure disclosed here can be useful because the dimensional precision of the structure can be realized at

a level of 100 μm or less, as mentioned above.

[0074] The present invention will now be explained in detail through the use of working examples, but is in no way limited to these examples.

(Embodiment 1)

In the present embodiment, a microturbine able to be used in a microfluid device was prepared. FIG. 4 (a) is a perspective view that explains the constitution of the microturbine main body. An image of this microturbine main body (a helical coil) can be produced by, for example, CAD or the like as 3D data that represents a three-dimensional shape. In addition, 3D data can be converted into slice data in a prescribed cross sectional direction by means of CAD or the like. This slice data is in, for example, STL format. By scanning a precision laser writing device on the basis of this slice data, it is possible to carry out laser writing that corresponds to the cross sectional shape of the microturbine main body. Moreover, in FIG. 4 (a), the shaft part that forms the axis of rotation of the turbine has been omitted in order to make the shape of the turbine main body easier to understand. In fact, a cylindrical shaft part having a diameter that fits a through hole in the center of the microturbine main body is combined with this microturbine main body. Here, a microturbine for electromagnetic induction type power generation can be formed by, for example, constituting the shown microturbine main body from a magnetic material and constituting the shaft part from a non-magnetic material.

[0075] Here, a composite fine structure formed of a gear-shaped microturbine main body shown in FIG. 4 (a) and a shaft part (not shown) was produced by using nanoparticles (average particle diameter 50 nm) of NiO, which is a non-magnetic material, as metal oxide nanoparticles. Ethylene glycol (EG) was used as a dispersion medium and reducing agent, and a thermosetting polyvinylpyrrolidone (PVP) was used as a laser-curable resin. In addition, a base solution was prepared by blending these components at a NiO nanoparticle : EG : PVP mass ratio of 46.9 : 42.9 : 10.2, and mixing by means of an ultrasonic stirrer. This base solution was uniformly coated on a glass substrate at a film thickness of approximately 9 μm by means of a spin coating method, and this base solution coating film was irradiated using an ultrashort pulse laser in the shape of a pattern corresponding to the desired microturbine structure. A femtosecond laser writing system (Photonic Professional GT produced by Nanoscribe) was used for the ultrashort pulse laser irradiation.

[0076] In the present embodiment, (A) the microturbine main body is produced by irradiating a paste-like base solution, which is formed of NiO nanoparticles and a thermosetting resin, with an ultrashort pulse laser so as to reduce the NiO nanoparticles to Ni, and then binding (including sintering or welding) these Ni nanoparticles. In addition, (B) the shaft part of the microturbine is produced by irradiating the (uncured)

paste-like base solution, which is formed of NiO nanoparticles and a thermosetting resin, with an ultrashort pulse laser so as to cure the thermosetting resin without modifying the NiO nanoparticles.

(A) The ultrashort pulse laser irradiation conditions used to form the microturbine main body were irradiating in air using an oscillating laser having a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz, focusing to a spot diameter of 1 μm using an objective lens having a numerical aperture of 0.75, and using a scanning speed of 1300 $\mu\text{m/s}$ and a pulse energy of 0.24 nJ.

(B) The ultrashort pulse laser irradiation conditions used to form the shaft part of the microturbine main body were irradiating in air using an oscillating laser having a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz, focusing to a spot diameter of 1 μm using an objective lens having a numerical aperture of 0.75, and using a scanning speed of 1300 $\mu\text{m/s}$ and a pulse energy of 0.06 nJ.

[0077] Moreover, this ultrashort pulse laser irradiation achieved direct writing using the above-mentioned femtosecond laser writing system, based on CAD data such as that shown in FIG. 4 (a). That is, the laser was first scanned under conditions (A) so as to fill the shape of the microturbine main body, thereby forming a microturbine main body formed of a sintered body of Ni nanoparticles, as shown in FIG. 4 (b). It was confirmed that the microturbine main body was constituted from a metallic nickel-containing phase and that a phase containing mainly NiO particles and a thermosetting resin was present at the periphery. Next, the hole in the center of the microturbine main body was scanned with the laser under conditions (B) so as to form the shaft part. It was confirmed that the shaft part was constituted from a phase containing mainly NiO particles and the thermosetting resin. The microturbine main body and shaft part were integrated with each other. It was confirmed that a composite fine structure formed of a microturbine main in body and a shaft part could be advantageously produced in this way. This microturbine main body (helical coil) had a diameter of 300 μm and a thickness of approximately 8 μm . In addition, the diameter of a cross section of the shaft part was approximately 80 μm , and the length in the axial direction was approximately 40 μm .

[0078] (Embodiment 2)

In the present embodiment, a three-dimensional micro-wire was produced. FIG. 5A is a perspective view (a) that explains the structure of this three-dimensional micro-wire, and a layered cross-sectional view (b) that explains the lamination pattern when producing this three-dimensional micro-wire using a lamination shaping method. In the present embodiment, a three-dimensional micro-wire is produced by coating a metal micro-wire with a mixed cured product of nanoparticles of an oxide of this metal and a

laser-curable resin, as shown in FIG. 5A.

First, CuO nanoparticles having an average particle diameter of 50 nm were used as metal oxide nanoparticles, ethylene glycol (EG) was used as a dispersion medium and reducing agent, and polyvinylpyrrolidone (PVP) was used as a laser-curable resin. In addition, a base solution was prepared by blending these components at a CuO nanoparticle : EG : PVP mass ratio of 60 : 27 : 13, and then mixing using an ultrasonic stirrer. This base solution was uniformly coated on a glass substrate at a film thickness of approximately 8 μm by means of a spin coating method, and this base solution coating film was irradiated using an ultrashort pulse laser in the shape of a pattern corresponding to the desired 3D wire structure.

[0079] In the present embodiment, (A) the micro-wire portion was produced by irradiating the paste-like (uncured) mixture of metal oxide nanoparticles and laser-curable resin using an ultrashort pulse laser, thereby reducing and binding (including sintering or welding) the metal oxide nanoparticles. In addition, (B) the coating portion was prepared by irradiating the paste-like mixture of metal oxide nanoparticles and laser-curable resin using an ultrashort pulse laser so as to cure the laser-curable resin without modifying the metal oxide nanoparticles.

[0080] (A) The ultrashort pulse laser irradiation conditions used to form the micro-wire portion were irradiating in air using an oscillating laser having a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz, focusing to a spot diameter of 1 μm using an objective lens having a numerical aperture of 0.75, and using a scanning speed of 1000 $\mu\text{m}/\text{s}$ and a pulse energy of 1.2 nJ.

(B) The ultrashort pulse laser irradiation conditions used to form the coating portion were irradiating in air using an oscillating laser having a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz, focusing to a spot diameter of 1 μm using an objective lens having a numerical aperture of 0.75, and using a scanning speed of 50 $\mu\text{m}/\text{s}$ and a pulse energy of 0.1 nJ.

[0081] Moreover, the ultrashort pulse laser radiation was carried out using a lamination shaping method. That is, in the cross section of the three-dimensional shape of the micro-wire shown in FIG. 5A (b), localized ultrashort pulse laser irradiation was carried out under appropriate conditions in order to form portions corresponding to a metal portion (A) (the micro-wire portion) and a metal oxide portion (B) (the coating portion) in that order from the bottom layer. In addition, the base solution coating and ultrashort pulse laser irradiation were repeatedly carried out when forming each layer. A three-dimensional micro-wire was obtained by sequentially overlaying and forming metal portions (A) and metal oxide portions (B) from the bottom layer to the top layer in the thickness direction, and then removing those parts of the paste-like mixture that had not been irradiated by the laser. FIG. 5B and FIG. 5C each show scanning electron

microscope images of 3D micro-wires produced in the present embodiment. It was confirmed that a composite fine structure formed of a micro-wire portion and a coating portion could be advantageously produced by the production method disclosed here.

[0082] (Embodiment 3)

Explanations will now be given of methods for separately forming a metal portion (A) and a metal oxide portion (B) by carrying out detailed investigations into the formation of metal portions (A) and metal oxide portions (B) in a variety of examples.

(Example 1)

Copper oxide (CuO) nanoparticles having an average particle diameter of 50 nm or less were prepared as metal oxide nanoparticles. Ethylene glycol (EG) was used as a dispersion medium and reducing agent, and a thermosetting polyvinylpyrrolidone (PVP) was used as a laser-curable resin. In addition, a base solution was prepared by blending these components at a CuO nanoparticle : EG : PVP mass ratio of 60 : 27 : 13, and then mixing using an ultrasonic stirrer.

[0083] This base solution was uniformly supplied to a glass substrate at a film thickness of approximately 8 μm using a spin coating method. Next, a fine pattern was irradiated on the base solution with an ultrashort pulse laser using a femtosecond laser writing system (Photonic Professional GT produced by Nanoscribe). The base solution was irradiated with prescribed writing patterns by using a laser oscillating at a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz as the ultrashort pulse laser, focusing to a spot diameter of 1 μm using an objective lens having a numerical aperture of 0.75, and altering the pulse energy at a scanning speed of 500 to 1000 $\mu\text{m/s}$. Following the ultrashort pulse laser irradiation, unreacted base solution was removed by rinsing the glass substrate with EG.

[0084] Following the laser irradiation, the glass substrate was observed with an optical microscope. FIG. 6 is a laser-drawn pattern (a) and a SEM image (b) of a glass substrate following laser irradiation. Moreover, the interval between scanning lines in the width direction in the laser-drawn pattern in FIG. 6 (a) is 100 μm . It can be confirmed that a fine pattern corresponding to the laser-drawn pattern (a) is directly drawn in the base solution following laser irradiation, as shown in FIG. 6 (b). The composition of the fine pattern portion was confirmed by X-Ray diffraction (XRD). As a result, diffraction peaks attributable to Cu, Cu₂O (copper (I) oxide) and CuO (copper (II) oxide) were confirmed. Therefore, it was understood that the fine pattern was formed by CuO nanoparticles being reduced to Cu₂O or Cu by the ultrashort pulse laser irradiation. In addition, this reduction occurs as CuO nanoparticles bind to each other and as CuO nanoparticles bind to the glass substrate, and it is thought that the fine pattern was formed on the substrate by the CuO nanoparticles being reduced by thermal reduction while simultaneously being sintered or melted (or partially melted).

Moreover, although specific data is not given, when this fine pattern was examined more closely, lustrous portions x having a metallic luster were observed in the center of the fine line in the width direction, and binding portions y having no metallic luster were observed at both edges of the fine line. Therefore, it was confirmed that this fine line was the composite fine structure disclosed here.

[0085] The line width of the formed fine line pattern was measured, and the relationship between the pulse energy and the line width is shown in FIG. 7. This pulse energy means the output energy per pulse. As shown in FIG. 7, the line width tends to increase as the pulse energy increases or the scanning speed decreases. It was confirmed that the minimum line width was 10 μm and the maximum line width was 28 μm in the present example. That is, it is surmised that the CuO nanoparticles are directly heated by irradiation energy from the ultrashort pulse laser and that CuO nanoparticles are also heated by heat diffusion or the like in a region that is broader than the region directly irradiated by the laser.

Therefore, it was understood that by irradiating the CuO nanoparticles with the ultrashort pulse laser, it was possible to form a fine line type fine structure by means of a thermal process.

[0086] (Example 2)

Next, fine line patterns were directly drawn using a base solution of CuO nanoparticles under the same conditions as those used in Example 1, except that the spot diameter of the ultrashort pulse laser was expanded from 1 μm to 23 μm and the scanning speed was slowed to 20 to 100 $\mu\text{m}/\text{s}$. In addition, the line width of the formed fine line pattern was measured, and the relationship between the pulse energy and the line width is shown in FIG. 8. In addition, FIG. 9 is optical microscope images of a fine structure formed using a pulse energy of 0.36 nJ and a scanning speed of 100 $\mu\text{m}/\text{s}$ (a) and a fine structure formed using a pulse energy of 1.2 nJ and a scanning speed of 20 $\mu\text{m}/\text{s}$ (b).

[0087] As shown in FIG. 8, the line width generally tends to increase as the pulse energy increases or the scanning speed decreases, in the same way as in Example 1. In the present example, however, the minimum line width was 5 μm and the maximum line width was 45 μm .

That is, in the present example, despite the scanning speed being slower than in Example 1, it was confirmed that the line width was approximately 5 μm , which is finer than the samples in Example 1, when the pulse energy was reduced to 0.36 nJ and the scanning speed was 50 or 100 $\mu\text{m}/\text{s}$. Moreover, as can be understood from FIG. 9 (a), a line width value of 5 to 10 μm , which is achieved at a pulse energy of 0.36 nJ, is smaller than the spot diameter of the irradiating ultrashort pulse laser, and a fine structure is formed in the vicinity of the center of the laser spot (on the scanning line).

In addition, a fine structure was not formed at the periphery of the laser spot, even at sites where the ultrashort pulse laser was irradiated a plurality of times. That is, under the laser irradiation conditions used in the present example, the energy imparted to the CuO nanoparticles, which can be adjusted by adjusting the intensity distribution of laser light within laser irradiation spots and the laser scanning speed, includes threshold values (boundaries) that define whether or not a pattern can be formed.

[0088] Therefore, the following matters were ascertained. That is, in cases where a femtosecond laser is used, if the scanning speed is too slow, the CuO nanoparticles absorb too much laser energy, in the same way as when a conventional nanosecond laser or the like is used, and the CuO nanoparticles can undergo thermal reduction or melting as a result of heat generation or heat diffusion. However, by, for example, using a femtosecond laser, slowing the scanning speed, irradiating with a laser having a sufficient intensity for the irradiation region only for an ultrashort period that is shorter than the average free time (that is, the minimum required quantity) and completely eliminating thermal effects, it is thought that it is possible to heat only the irradiation region with the prescribed laser intensity and energy. It can be said that this means that by regulating the laser intensity, laser irradiation time (which can include the scanning speed) and the like, with the minimum quantity required for thermal reduction being a threshold value, it is possible to heat and thermally reduce only a prescribed single CuO nanoparticle and suppress thermal effects around the nanoparticle.

[0089] Moreover, it was understood that if the pulse energy is increased to 0.96 nJ or 1.2 nJ, the line width also increases, and that if the scanning speed is reduced to 20 $\mu\text{m/s}$, the line width becomes broader than that of the samples in Example 1. Here, as shown in FIG. 9 (b), for example, it appears as if the CuO nanoparticles have melted, and there is a great deal of variation in the line width.

Therefore, it was understood that a fine structure having a dimension of approximately 5 μm could be formed when reducing metal oxide (CuO in this case) nanoparticles in air using an ultrashort pulse laser. In addition, this dimension can be adjusted by adjusting the energy imparted by the laser by adjusting, for example, the writing speed or laser output, and it was confirmed that metal oxide reduction and writing could be achieved with high-efficiency.

[0090] (Example 3)

Fine structures formed of fine patterns obtained by reducing CuO nanoparticles were formed under the same conditions as those in Example 1 (a spot diameter of 1 μm), except that the scanning speed and pulse energy were variously altered. In addition, the composition of the fine structure was investigated by XRD in cases where a fine structure could be formed. These results are shown in Table 1.

Moreover, the expressions in Table 1 mean the following.

"x" means that a fine structure was not formed from the CuO nanoparticles or that a fine structure was washed away by the EG.

[0091] "CuO" means that XRD peaks were mainly attributable to CuO. That is, this means that under these conditions, metal oxide portions (B) are mainly formed.

"CuO-rich" means that XRD peaks were mainly attributable to CuO, but that peaks attributable to Cu_2O were also detected. That is, this means that under these conditions, metal oxide portions (B) are mainly formed and third metal oxide portions (B") are formed.

" Cu_2O -rich" means that XRD peaks were mainly attributable to Cu_2O , but that peaks attributable to Cu were also detected. That is, this means that under these conditions, metal portions (A) are mainly formed, and these metal portions are phases containing mainly Cu_2O .

"Cu-rich" means that XRD peaks were mainly attributable to Cu, but that peaks attributable to Cu_2O were also detected. That is, this means that under these conditions, metal portions (A) are mainly formed, and metallization occurred more advantageously.

" Cu_2O +Cu" means that peaks attributable to Cu_2O and Cu among the XRD peaks were present at approximately similar proportions. That is, this means that under these conditions, metal portions (A) are mainly formed.

"CuO-rich (melted)" means that the XRD peaks were the same as those for the "CuO-rich" described above, but that the nanoparticles melted, making line width control difficult. That is, this means that under these conditions, metal oxide portions (B) are mainly formed and second metal oxide portions (B') are formed.

[0092]

[Table 1]

Table 1

Scanning speed ($\mu\text{m/s}$)	Pulse energy (nJ)					
	0.01	0.05	0.1	0.2	0.6	1.2
20	×	CuO _{-rich}	CuO _{-rich}	CuO _{-rich}	Cu ₂ O _{-rich}	CuO _{-rich} (melted)
50	×	CuO _{-rich}	CuO _{-rich}	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}
100	×	CuO	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}
500	×	CuO	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu _{-rich}
1000	×	CuO	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu ₂ O+CuO	Cu _{-rich}
1500	×	CuO	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu ₂ O _{-rich}	Cu _{-rich}
2000	×	CuO	Cu ₂ O _{-rich}	Cu _{-rich}	Cu _{-rich}	Cu _{-rich}

[0093] As shown in Table 1, when the pulse energy was 0.01 nJ, a fine structure could not be formed at any scanning speed, and the CuO nanoparticles were washed away by the EG. However, when the pulse energy exceeded 0.01 nJ, it was confirmed that fine structures could be formed at almost any scanning speed. In addition, even in cases where a fine structure could be formed, it was confirmed that by adjusting the scanning speed and pulse energy, it was possible to control the composition of the fine structure and the proportions of portions therein. That is, it was understood that it was possible to form a fine structure by controlling the proportions of a metal oxide (CuO in this case) and a reduced product thereof. Here, it was understood that, in general terms, by relatively increasing the pulse energy and lowering the scanning speed, it was possible to facilitate reduction of the metal oxide and easy to obtain a fine structure having a high degree of reduction.

[0094] Here, in the case of samples obtained using a pulse energy of 0.05 nJ, reduction of the metal oxide nanoparticles tended to progress as the scanning speed was lowered, whereas in the case of samples obtained using pulse energies of 0.1 to 1.2 nJ, the metal oxide was reduced as the scanning speed was increased. In addition, in a case where the pulse energy was 1.2 nJ and the scanning speed was 20 $\mu\text{m/s}$, the CuO nanoparticles completely melted and it was difficult to form a fine structure having the desired line width (for example, see FIG. 9 (b)). Therefore, because the metal oxide nanoparticles were subjected to high intensity pulse energy in samples obtained using

pulse energies of 0.1 to 1.2 nJ, it was predicted that metal nanoparticles that had once been reduced from a metal oxide (CuO), which is a non-metal, to a semiconductor or metal (Cu₂O or Cu) were re-oxidized to a metal oxide or semiconductor (CuO or Cu₂O) in cases where the scanning speed was slow. Therefore, reduction of the metal oxide does not depend merely on the total quantity of energy subjected to the nanoparticles, and it was confirmed that by selecting the pulse energy and scanning speed in view of this re-oxidation, it is possible to more reliably control the proportions of the metal oxide and reduced product. In addition, by controlling the pulse energy and scanning speed, as mentioned above, a metal portion (a portion constituted mainly from Cu in this case) and a metal oxide portion (a portion constituted mainly from CuO and/or Cu₂O in this case) can be formed locally as separate portions in the fine structure.

- [0095] Moreover, under the conditions represented by "Cu₂O-rich", "Cu-rich" and "Cu₂O+Cu" in Table 1, a metal portion (A) is formed in the technique disclosed here. However, under conditions represented by "Cu₂O-rich", for example, even if a metal portion (A) is formed, a phase containing mainly Cu₂O, which is a semiconductor, is formed. With regard to this matter, the metal portion (A) disclosed here can be ascertained as, for example, a second metal portion (A') (for example, a portion containing mainly a semiconductor), which is understood to also be a metal re-oxidation portion.
- [0096] In addition, within the laser irradiation conditions described above, a fine structure formed under conditions whereby mainly metal portions (A) are formed is such that metal oxide portions (B) are incidentally formed at the periphery of the metal portions (A). Therefore, these laser irradiation conditions are such that the composite fine structure disclosed here can be produced only under these conditions. Meanwhile, in a fine structure formed under conditions whereby mainly metal oxide portions (B) are formed, metal portions (A) can be formed in, for example, portions in which the same location has been irradiated twice by the laser. Therefore, with regard to laser irradiation conditions under which mainly metal oxide portions (B) are formed, the composite fine structure disclosed here can be produced by (1) repeatedly carrying out laser irradiation and (2) combining with formation achieved by means of laser irradiation conditions under which mainly metal portions are formed.
- [0097] The scanning speed and pulse energy combinations shown in Table 1 are an example of preset conditions for an ultrashort pulse laser. A person skilled in the art could understand that by using, as critical values, conditions obtained by combining scanning speeds and pulse energies which are shown in the table as being able to produce a composite fine structure, it would be possible to produce a composite fine structure under laser irradiation conditions that include these conditions. Similarly, a person

skilled in the art could understand that by using, as critical values, conditions obtained by combining scanning speeds and pulse energies which are shown as being able to produce a structure (a composite fine structure) that includes phases represented by "CuO", "CuO-rich", "Cu₂O-rich", "Cu-rich", "Cu₂O+Cu" and "CuO-rich (melted)" in the table, it would be possible to produce a variety of structures (composite fine structures) under laser irradiation conditions that include these conditions. Similar matters can be understood from Table 2 and Table 3 below. Fine structures including any metallic element, and having a composition organization where oxides of the metallic element varying in the oxidation state (or a reduction degree, composition) is arbitrarily combined, can be produced.

[0098] (Example 4-1)

Fine structures each formed of a combination of fine line patterns were produced under the same conditions as those used in Example 1, except that the pulse energy was 1.2 nJ, the spot diameter was 1 μm and the scanning speed was 500 $\mu\text{m/s}$ or 1000 $\mu\text{m/s}$. Under these conditions, it is possible to produce fine structures having compositions mainly made of Cu₂O-rich or Cu-rich. Here, with regard to these compositions, three band-shaped fine structures each having a length of 100 μm and a width of 160 to 600 μm were formed by drawing fine lines without intervals. This composite fine structure is constituted mainly from phases classified as metal portions (A), with metal portions (B) being present at both edges in the width direction.

Resistance measurement electrodes were disposed at both edges in the length direction of the fine structure obtained in this way, and the electrical resistance was measured using a two-point method. These results are shown in FIG. 10.

[0099] As shown in FIG. 10, the electrical resistance of the fine structure decreases as the line width increases. In addition, these resistance values were 11 to 54 Ω for Cu-rich structures and 0.22 to 8.9 M Ω for Cu₂O-rich structures, and it was confirmed that the electrical resistance of the fine structure could be controlled by adjusting the composition. Moreover, if it is taken that the film thickness of the fine structure is approximately 8 μm , the resistivity of the structure has a minimum value of 528 $\mu\Omega\text{m}$ in a Cu-rich structure. It is thought that this resistivity is high because the formed fine structure is relatively porous, and it is thought that the resistivity can be lowered by improving the concentration of CuO nanoparticles or the method of supply.

[0100] (Example 4-2)

Next, square composite fine structures measuring 150 μm x 150 μm were formed under two sets of conditions, and the resistance-temperature characteristics of these composite fine structures were evaluated. Specifically, two Cu electrodes having an inter-electrode distance of 100 μm were produced by forming Cu thin films on a glass substrate using a lithography method, as shown in FIG. 14 (a). Next, composite fine

structures (1) and (2) were formed by writing a pattern measuring $150\ \mu\text{m} \times 150\ \mu\text{m}$ under the laser irradiation conditions shown by conditions (1) and (2) in such a way as to bridge the two Cu electrodes. Moreover, condition (1) is a condition under which a composite fine structure having mainly a Cu-rich composition, which is a metal portion, is formed. This Cu-rich composition is formed mainly of a phase in which the content of Cu is 50% or higher. In addition, condition (2) is a condition under which a composite fine structure having mainly a Cu_2O -rich composition, which is a metal portion (which is ascertained as being, for example, a semiconductor-rich portion or the like), is formed. This Cu_2O -rich composition is formed mainly of a phase in which the content of Cu_2O is 50% or higher. In these composite fine structures, a metal oxide portion (B) is incidentally formed at the periphery of the square metal portion (A). For reference purposes, an SEM image of the composite fine structure formed under condition (2) is shown in FIG. 14 (b). Next, fine elements (1) and (2) for evaluation were produced by connecting a Pt lead wire to the Cu electrodes of composite fine structures (1) and (2).

[0101] Condition (1); Pulse energy: 1.2 nJ

Spot diameter: $1\ \mu\text{m}$

Scanning speed: $500\ \mu\text{m/s}$

Condition (2); Pulse energy: 1.2 nJ

Spot diameter: $1\ \mu\text{m}$

Scanning speed: $1000\ \mu\text{m/s}$

[0102] The resistance-temperature characteristics of the composite fine structures (1) and (2) were evaluated by mounting these fine elements on a hot plate and passing a current while altering the temperature of the composite fine structures within the range of 30°C to 70°C . These results are shown in FIG. 15 (a) and (b), respectively.

As shown in FIG. 15 (a), the resistance-temperature coefficient of the composite fine structure (1) having a Cu-rich composition obtained in this example was approximately $1.0 \times 10^{-3}/^\circ\text{C}$. This value does not match the (theoretical) resistance-temperature coefficient of Cu, but was confirmed as being a positive resistance-temperature coefficient seen in metal materials. Therefore, it was understood that this composite fine structure (1) could be used as an electrically conductive member, such as a wire or electrode. Meanwhile, the resistance-temperature coefficient of the composite fine structure (2) having a Cu_2O -rich composition was approximately $-15 \times 10^{-3}/^\circ\text{C}$, as shown in FIG. 15 (b), and the composite fine structure (2) is classified as a "metal portion" in the technique disclosed here, but was confirmed as exhibiting a high negative resistance-temperature coefficient seen in semiconductor materials. Therefore, it was understood that this composite fine structure (2) could be used as, for example, a high sensitivity temperature sensor in low temperature regions of approximately 30°C

to 70°C. Moreover, a person skilled in the art could understand that in the fine element (2) shown in FIG. 14 (a) and (b), the Cu electrode portion produced by lithography in the present example could be formed by laser irradiation carried out under condition (1). Therefore, it was understood that a greater part of a temperature sensor can be simply produced using the composite fine structure disclosed here. In addition, a person skilled in the art could understand that this type of composite fine structure could also be used in an acceleration sensor, a flow rate sensor, a stress sensor, or the like.

[0103] Therefore, according to the technique disclosed here, it was confirmed that even in a composite fine structure formed mainly of a metal portion (A), the composition of the structure could be reliably separated into a Cu-rich composition and a Cu₂O-rich composition, which have different physical properties, at micron level dimensions. In addition, it was understood that by utilizing the physical properties inherent in these compositions, composite fine structures having a variety of functions can be produced.

[0104] (Example 5)

Next, a fine structure was produced by using NiO nanoparticles having an average particle diameter of 50 nm instead of CuO nanoparticles. EG was used as a dispersion medium and reducing agent, and PVP was used as a laser-curable resin. In addition, a base solution was prepared by blending these components at a NiO nanoparticle : EG : PVP mass ratio of 46.9 : 42.9 : 10.2, and mixing by means of an ultrasonic stirrer. This base solution was uniformly coated on a glass substrate at a film thickness of approximately 9 µm by means of a spin coating method, and this base solution coating film was irradiated using an ultrashort pulse laser in the shape of a fine pattern. The base solution was irradiated with prescribed writing patterns by using a laser oscillating at a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz as the ultrashort pulse laser, focusing to a spot diameter of 1 µm using an objective lens having a numerical aperture of 0.75, and altering the pulse energy to the six values shown in Table 2 below at a scanning speed of 100 to 1500 µm/s. Following the ultrashort pulse laser irradiation, unreacted base solution was removed by rinsing the glass substrate with EG.

[0105] In this way, fine structures formed of fine patterns were formed by reducing the NiO nanoparticles. In addition, the compositions of the fine structures were investigated by XRD in those cases where a fine structure could be formed. These results are shown in Table 2.

Moreover, the expressions in Table 2 mean the following.

"x" means that a fine structure was not formed from the NiO nanoparticles or that a fine structure was washed away by the EG.

"NiO" means that XRD peaks were mainly attributable to NiO. That is, this means

that under these conditions, metal oxide portions (B) are mainly formed.

"NiO+Ni" means that peaks attributable to NiO and Ni among the XRD peaks were present at approximately similar proportions. That is, this means that under these conditions, metal portions (A) are mainly formed.

"NiO-rich (melted)" means that XRD peaks were mainly attributable to NiO, but that peaks attributable to Ni were also detected, and the nanoparticles melted, making line width control difficult. That is, under these conditions, metal portions (A) are mainly formed, but metal portions containing re-oxidized portions are formed.

[0106] [Table 2]

Table 2

Scanning speed ($\mu\text{m/s}$)	Pulse energy (nJ)					
	0.01	0.06	0.24	0.48	0.6	1.2
100	×	NiO	NiO	NiO	NiO	NiO-rich (melted)
500	×	NiO	NiO+Ni	NiO+Ni	NiO+Ni	NiO-rich (melted)
1000	×	NiO	NiO+Ni	NiO+Ni	NiO+Ni	NiO-rich (melted)
1500	×	NiO	NiO+Ni	NiO+Ni	NiO+Ni	NiO-rich (melted)

[0107] As shown in Table 2, when the pulse energy was 0.01 nJ, a fine structure could not be formed at any scanning speed, and the NiO nanoparticles were washed away by the EG. In addition, in cases where the pulse energy was 1.2 nJ, the NiO nanoparticles completely melted and it was difficult to form a fine structure having the desired line width. In addition, in cases where the pulse energy fell within the range of greater than 0.01 nJ but less than 1.2 nJ, it was confirmed that a fine structure could be formed at almost any scanning speed.

In addition, in cases where a fine structure was formed, it was confirmed that by adjusting the scanning speed and the pulse energy, it was possible to control the composition of the fine structure and the proportions of the portions therein. That is, it was understood that it was possible to form a fine structure by controlling the proportions of a metal oxide (NiO in this case) and a reduced product thereof (Ni).

[0108] Next, the relationship between the scanning speed and the composition of the fine structure was investigated by slightly altering the scanning speed at a pulse energy of 0.24 nJ. The scanning speed was altered to 200 $\mu\text{m/s}$ or higher, at which a "NiO+Ni" composition, which is mainly a metal portion (A), could be reliably obtained. These

results are shown in FIG. 11. In FIG. 11, the vertical axis shows $I_{\text{Ni}(111)}/I_{\text{NiO}(200)}$, which is the diffraction intensity ratio of a diffraction peak from the Ni (111) face relative to the diffraction peak from the NiO (200) face in an XRD pattern of a formed fine structure, and as this value increases, more NiO is reduced to Ni.

[0109] As is clear from FIG. 11, it can be understood that in this example, the proportion of Ni in the fine structure is at a maximum when the scanning speed is close to 1300 $\mu\text{m/s}$, and the proportion of Ni decreases as the scanning speed deviates above or below 1300 $\mu\text{m/s}$. In view of the results obtained in Examples 1 to 4 above, it is thought that in cases where the scanning speed is greater than 1300 $\mu\text{m/s}$ in this example, the pulse energy supplied from the ultrashort pulse laser to the NiO nanoparticles is not sufficient and unreduced NiO, which has not been reduced to Ni, remains in the fine structure. In addition, in cases where the scanning speed is lower than 1300 $\mu\text{m/s}$, it is thought that the pulse energy supplied from the ultrashort pulse laser to the NiO nanoparticles is greater than that required for thermal reduction of NiO, and reduced Ni is again oxidized to NiO by the excess energy.

[0110] Therefore, it is surmised that the NiO is in an unoxidized state in cases where the pulse energy is 0.06 nJ in Table 2, and it is thought that in cases where the pulse energy is 0.48 nJ or higher, it is possible that the NiO is re-oxidized NiO in cases where the scanning speed is low and is unoxidized NiO in cases where the scanning speed is high.

In addition, even if NiO having the same XRD diffraction results is identified, because NiO in an unreduced state has not been sufficiently heated, it is thought that PVP will be present around the NiO and contribute to the formation of the fine structure. Meanwhile, because re-oxidized NiO is in a sufficiently heated state, it is thought that starting material NiO nanoparticles will be welded or sintered to each other and that PVP contained in the base solution will be lost.

[0111] In addition, even in a fine structure formed mainly of a metal portion (A), it can be confirmed that by controlling the laser irradiation conditions, it is possible to finally control the composition in the metal portion (A). Moreover, within the laser irradiation conditions described above, a fine structure formed under conditions whereby mainly metal portions (A) are formed is such that metal oxide portions (B) are incidentally formed at the periphery of the metal portions (A). Therefore, these laser irradiation conditions are such that the composite fine structure disclosed here can be produced only under these conditions. Meanwhile, in a fine structure formed under conditions whereby mainly metal oxide portions (B) are formed, metal portions (A) can be formed in, for example, portions in which the same location has been irradiated twice by the laser. Therefore, with regard to laser irradiation conditions under which mainly metal oxide portions (B) are formed, the composite fine structure disclosed here can be

produced by (1) repeatedly carrying out laser irradiation and (2) combining with formation achieved by means of laser irradiation conditions under which mainly metal portions are formed. Therefore, it is understood that it is possible to precisely form a micron sized structural member made of Ni (a magnetic material) and NiO (a non-magnetic material). This type of structure can be advantageously realized as, for example, a micron sized non-magnetic actuator or the like.

[0112] (Example 6)

Fine structures formed of fine patterns obtained by reducing NiO nanoparticles were formed under the same conditions as those used in Example 5, except that the scanning speed was more precisely altered in cases where the pulse energy was 0.48 nJ in addition to those cases in Example 5 in which the pulse energy was 0.24 nJ. In addition, the line widths of the formed structures were measured, and the results are shown in FIG. 12.

As shown in FIG. 12, it was understood that in cases where the pulse energy was 0.24 nJ or 0.48 nJ when reducing the NiO nanoparticles, the line width was stably reduced, with no significant dependence on scanning speed. For example, at scanning speeds of 100 $\mu\text{m/s}$ and 500 $\mu\text{m/s}$, the quantities of ultrashort pulse laser energy irradiated on the NiO nanoparticles are completely different, but it was understood that the line width was maintained at approximately 15 μm or less and that fine structures having fine line widths could be stably obtained. This is thought to be because the quantity of energy supplied in a single laser pulse is small, meaning that the degree of heating of the NiO nanoparticles is suppressed, and when the nanoparticles are irradiated with the next laser pulse, the once heated NiO nanoparticles have cooled, meaning that heat accumulation and runaway heat storage do not occur. In the present example, in cases where the pulse energy is 0.24 nJ in particular, no significant difference in terms of line width is seen between a case in which the scanning speed is 1500 $\mu\text{m/s}$ and a case in which the scanning speed is 100 $\mu\text{m/s}$. Meanwhile, it was understood that in cases where the pulse energy is 0.48 nJ, excessive energy is supplied and the line width tends to increase at scanning speeds of approximately 300 $\mu\text{m/s}$ or lower, but line widths could be stably maintained irrespective of scanning speed at scanning speeds of 400 $\mu\text{m/s}$ or higher. In addition, in cases where line widths are stable in this way, it is thought that the line widths increase as the pulse energy increases.

[0113] (Example 7)

Furthermore, fine structures were formed using TiO_2 nanoparticles having an average particle diameter of 20 nm as metal oxide nanoparticles. EG was used as a dispersion medium and reducing agent, and PVP was used as a laser-curable resin. In addition, a base solution was prepared by blending these components at a TiO_2 nanoparticle : EG :

PVP mass ratio of 30 : 63.5 : 6.5, and mixing by means of an ultrasonic stirrer. This base solution was uniformly coated on a glass substrate at a film thickness of approximately 7 μm by means of a spin coating method, and this base solution coating film was irradiated using an ultrashort pulse laser in the shape of a fine pattern. The ultrashort pulse laser irradiation conditions were irradiating in air using an oscillating laser having a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz, and focusing to a spot diameter of 1 μm using an objective lens having a numerical aperture of 0.75. Moreover, the ultrashort pulse laser irradiated a prescribed pattern using a pulse energy of 1.0 nJ, 1.1 nJ or 1.2 nJ and a scanning speed of 30 $\mu\text{m/s}$. In addition, when the pulse energy was 1.1 nJ, a fine structure was formed even when the scanning speed was altered to 20 $\mu\text{m/s}$ or 40 $\mu\text{m/s}$. Following the ultrashort pulse laser irradiation, unreacted base solution was removed by rinsing the glass substrate with EG.

[0114] As a result, it was confirmed that in all cases where the pulse energy was 1.0 nJ, 1.1 nJ or 1.2 nJ, a structure was formed on the substrate. In such cases the minimum line width was 20 μm and the maximum line width was 40 μm .

Moreover, when the compositions of the formed fine structures were confirmed by XRD analysis, it was understood that the composition of a structure obtained at a pulse energy of 1.0 nJ and a scanning speed of 30 $\mu\text{m/s}$ was formed of a single TiO_2 phase, that the TiO_2 nanoparticles had not been reduced, and that a structure had been formed by the PVP, which is a laser-curable resin, being cured. That is, a fine structure containing a metal portion and a metal oxide portion, as disclosed here, was not formed. Meanwhile, it was understood that the composition of a structure obtained at a pulse energy of 1.1 nJ or 1.2 nJ contained TiO and TiO_2 , and that a fine structure, in which at least some of the TiO_2 nanoparticles had been reduced to TiO and bound to each other, was formed. That is, it can be said that a composite fine structure formed of a reduced portion and a non-reduced portion was produced. Among metal oxides, TiO_2 has a low standard formation free energy and is not readily reduced. Therefore, it was confirmed that reduction could be brought about stably at a relatively low scanning speed and that a fine structure having a fine line width could be stably formed.

[0115] (Example 8)

Furthermore, fine structures were formed using, as metal oxide nanoparticles, Cu/CuO core-shell type nanoparticles in which Cu was the core and CuO was the shell (manufactured by Ionic Liquids Technologies GmbH, particle diameter < 50 nm). EG was used as a dispersion medium and reducing agent, and PVP was used as a laser-curable resin. In addition, a base solution was prepared by blending these components at a core-shell type nanoparticle : EG : PVP mass ratio of 60 : 27 : 13, and mixing by means of an ultrasonic stirrer. This base solution was uniformly coated on a glass

substrate at a film thickness of approximately 7 μm by means of a spin coating method, and this base solution coating film was irradiated using an ultrashort pulse laser in the shape of a fine pattern. The ultrashort pulse laser irradiation conditions were irradiating in air using an oscillating laser having a wavelength of 780 nm, a pulse duration of 120 fs and a cyclic frequency of 80 MHz, and focusing to a spot diameter of 1 μm using an objective lens having a numerical aperture of 0.75. Moreover, fine structures were formed by irradiating the base liquid at a prescribed pattern using an ultrashort pulse laser at four pulse energies, namely 0.01 nJ, 0.05 nJ, 0.6 nJ and 1.2 nJ, and six scanning speeds between 50 $\mu\text{m/s}$ and 2000 $\mu\text{m/s}$. Following the ultrashort pulse laser irradiation, unreacted base solution was removed by rinsing the glass substrate with EG.

[0116] As a result, it was confirmed that a fine structure was formed on a substrate at all pulse energies and scanning speeds. In these cases the minimum line width was 10 μm and the maximum line width was 60 μm . The compositions of the formed fine structures were confirmed by XRD analysis, and the results are shown in Table 3. Moreover, the expressions in Table 3 mean the following.

"Y" indicates conditions under which peaks attributable to CuO were detected in the XRD diffraction peaks. Moreover, although not explicitly indicated, conditions shown by "Y" include cases where peaks attributable to Cu were detected and cases where peaks attributable to Cu were not detected. The case where peaks attributable to Cu were not detected were conditions where the scanning speed was 50 $\mu\text{m/s}$ and the pulse energy was 1.2 nJ.

"N" indicates that peaks attributable to CuO were not detected in the XRD diffraction peaks.

[0117] [Table 3]

Table 3

Scanning speed ($\mu\text{m/s}$)	Pulse energy (nJ)			
	0.01	0.05	0.6	1.2
50	Y	Y	Y	Y
100	Y	Y	Y	Y
500	Y	Y	Y	Y
1000	Y	Y	N	N
1500	Y	Y	N	N
2000	Y	Y	N	Y

- [0118] By comparing Table 3 with Example 3 in Table 1, it was understood that because core-shell type nanoparticles were used in the present example, it was possible to form a metal oxide portion at a lower pulse energy. In addition, in cases where the pulse energy was 0.6 nJ or higher and the scanning speed was 1000 $\mu\text{m/s}$ or higher, the CuO in the shell portion was almost completely reduced and it was possible to obtain a fine structure formed almost entirely of Cu particles (that is, containing almost no CuO). However, in cases where the pulse energy was 1.2 nJ or higher and the scanning speed was 2000 $\mu\text{m/s}$ or higher, it could be confirmed that the CuO shell portion could remain because the energy supplied to the core-shell type nanoparticles was reduced. Moreover, it could be confirmed that in fine structures formed by irradiating with the ultrashort pulse laser under irradiation conditions that produce the result "N" in Table 1, core-shell type particles in which the CuO shell portion remains are present in extremely small quantities at the periphery of a heat-affected portion caused by the laser irradiation. That is, it was confirmed that such fine structures are composite fine structures.
- [0119] In this composite fine structure, the core portion of the core-shell type structure is Cu, and most of the shell portion is reduced to Cu. In other words, CuO is not detected in most parts of the composite fine structure, which is constituted only from Cu. Therefore, it can be confirmed that a composite fine structure having particularly excellent electrical conductivity can be obtained by using the technique disclosed here. In addition, it was confirmed that a composite fine structure can be formed even using core-shell type nanoparticles.
- [0120] In addition, the technique disclosed here also provides an additive manufacturing apparatus (also known as a three-dimensional molding device or a three-dimensional printing apparatus) 1. The additive manufacturing apparatus may preferably use for manufacturing a composite fine structure (a three-dimensional molded article) which contains a metal oxide portion (B) containing metal oxide nanoparticles, and a metal portion (A) in which at least some of the metal oxide nanoparticles are reduced and directly bonded to each other, the dimension of at least one of the metal oxide portion (B) and the metal portion (A) being 100 μm or less. FIG. 16 is a schematic view that shows the constitution an additive manufacturing apparatus according to one embodiment. The apparatus 1 is provided with: a laser oscillation device 10 and a control device 20. The laser oscillation device 10 generates an ultrashort pulse laser irradiated to a metal oxide nanoparticle-containing liquid 100, which contains the metal oxide nanoparticles and a laser-curable resin that is cured by being irradiated with laser light. The control device 20 controls laser oscillation conditions for the laser oscillation device 10.
- [0121] It is not limited by the following, in order to facilitate molding, but the apparatus 1

may be provided with a stage 30, to which the metal oxide nanoparticle-containing liquid 100 is supplied and which is used in order to carry out molding. Furthermore, the apparatus 1 may be provided with a supply device (not shown) that supplies the metal oxide nanoparticle-containing liquid 100 to the stage 30. In addition, the apparatus 1 may be provided with an image pick-up device 40 formed of a CCD camera or the like in order to confirm the state of molding.

[0122] The control device 20 is provided with a first storage unit 21, a second storage unit 22 and a laser oscillation conditions setting unit 23.

The first storage unit 21 stores cross sectional image data, which are obtained by slicing a three-dimensional article to be molded into a plurality of cross sectional layers and which include at least positional information of a site constituted from the metal portion (A) in each of the cross sectional layers. The cross sectional image data may include positional information of a site constituted from the metal oxide portion (B) and may include positional information of a site constituted from a second metal portion (A'), which exhibits semiconductor characteristics.

The second storage unit 22 stores at least previously acquired laser irradiation conditions for forming the metal portion (A) by reducing the metal oxide nanoparticles. The second storage unit may store laser irradiation conditions for forming the metal oxide portion (B) by curing a laser -curable resin without reducing the metal oxide nanoparticles, and may store laser irradiation conditions for forming the second metal portion (A'), which is obtained by reducing metal oxide nanoparticles and which exhibits semiconductor characteristics.

[0123] The laser oscillation conditions setting unit 23 is configured so as to control the position at which the metal oxide nanoparticle-containing liquid is irradiated with the laser oscillated by the laser oscillation device based on the cross sectional image data, and so as to oscillate the laser under conditions for forming the metal portion (A) at a site to be constituted from the metal portion (A) in the cross sectional layer. The laser oscillation conditions setting unit may be constituted so that the laser is oscillated under conditions for forming the metal oxide portion (B) at a site to be constituted from the metal oxide portion (B) in the cross sectional layer. In addition, the laser oscillation conditions setting unit may be constituted so that the laser is oscillated under conditions for forming the second metal portion (A') at a site to be constituted from the second metal portion (A'). In a constitution in which a stage 30 is provided, the laser oscillation conditions setting unit 23 may be configured so as to control the position at which the laser is irradiated by adjusting the relative positions of the stage 30 and the laser oscillation device 10.

[0124] The laser oscillation device 10 is not particularly limited, and it is possible to use a variety of publicly known laser oscillators able to transmit the ultrashort pulse laser

disclosed here. The laser medium is not particularly limited, and it is possible to use, for example, a solid state laser that uses crystals of titanium sapphire, chromium forsterite, Yb: YAG or Yb: KGW as a laser medium, a fiber laser that uses, as a laser medium, a glass fiber obtained by doping erbium (Er) or ytterbium (Yb) in a core, or a dye laser (liquid laser) that uses an organic dye solution as a medium. The laser oscillation device 10 may, as appropriate, be provided with an optical system constituted from a mirror 12a, a beam expander 14, a half mirror 12b, an object lens 16, and the like.

[0125] The control device 20, first storage unit 21, second storage unit 22 and laser oscillation conditions setting unit 23 may be constituted from hardware (a processor etc.) using a logic circuit formed from an integrated circuit or the like, but may also be constituted in such a way that a CPU is functionally implemented by running a computer program. The control device 20 may also be provided with ROM, in which a program or the like to be run by a CPU is stored, RAM, and the like. Moreover, the computer program may be configured in such a way that the program can be transmitted to a CPU via an arbitrary transmissible transmission medium (a wired or wireless communication means or the like). In addition, the computer program may be in the form of data signals contained in carrier waves that are electronically transmitted.

[0126] The stage 30 may be constituted in such a way that, for example, the positional relationship with the laser irradiation position (spot) that is oscillated by the laser oscillation device 10 can be moved in a three-dimensional manner. The stage 30 may be moved in the X axis direction and Y axis direction in the X-Y plane by means of, for example, a transfer device (not shown). In addition, the stage 30 may be connected to a transfer device (not shown) capable of moving the stage in the Z axis direction. The transfer device may be, for example, an actuator able to precisely determine positions at the sub micron order (for example, a precision of approximately 100 nm) in one axis, two axes or three axes (for example, a piezoelectric actuator that uses a piezoelectric material). In addition, the transfer device may be constituted from, for example, a holder that supports the stage 30, a slide rail which extends in the prescribed direction of movement and which engages in a freely sliding manner with the holder, and a motor that drives the holder. The transfer device may have a constitution obtained by combining a plurality of these.

[0127] The supply device may be a variety of publicly known coating/supply devices. For example, it is possible to use a supply device that uses a variety of methods, such as a casting method, a doctor blade method, a dip coating method, a spin coating method, an electrophoresis method, a spraying method, an ink jet method, a screen printing method or a gravure printing method.

Preferred embodiments of the present invention have been explained above, but the

matters mentioned above are not limiting matters and may, of course, be variously modified.

Claims

- [Claim 1] A composite fine structure comprising:
a metal oxide portion containing metal oxide nanoparticles; and
a metal portion in which at least some of the metal oxide nanoparticles are reduced and directly bonded to each other,
wherein the metal oxide portion and the metal portion are integrated with each other, and the dimension of at least one of the metal oxide portion and the metal portion is 100 μm or less.
- [Claim 2] The composite fine structure according to claim 1, wherein the metal oxide nanoparticles contain oxides of at least one of metal element selected from the group consisting of gold (Au), silver (Ag), copper (Cu), nickel (Ni), iron (Fe) and titanium (Ti).
- [Claim 3] The composite fine structure according to claim 1 or claim 2, wherein the metal oxide portion further contains a laser-curable resin, and contains a first metal oxide portion in which at least some of the metal oxide nanoparticles are bonded to each other by the laser-curable resin.
- [Claim 4] The composite fine structure according to any one of claims 1 to 3, wherein the metal oxide portion contains a second metal oxide portion in which at least some of the metal oxide nanoparticles are directly bonded to each other.
- [Claim 5] The composite fine structure according to claim 3 or 4, wherein the metal oxide portion contains the first metal oxide portion and the second metal oxide portion, and the first metal oxide portion accounts for 50 vol.% or more of a total volume of the first metal oxide portion and the second metal oxide portion.
- [Claim 6] The composite fine structure according to any one of claims 1 to 5, wherein the metal oxide nanoparticles are nanoparticles that contain a metal oxide in at least a part thereof.
- [Claim 7] The composite fine structure according to claim 6, wherein the metal oxide nanoparticles are core-shell type nanoparticles that contain a shell formed of a metal oxide on at least a part of a surface of core particles.
- [Claim 8] A microturbine component comprising the composite fine structure according to any one of claims 1 to 7,
the microturbine component further comprising: a gear-shaped microturbine main body; and a shaft part that forms an axis of rotation of the microturbine main body, wherein the microturbine main body is

constituted from the metal portion containing nickel, and the shaft part is constituted from the metal oxide portion containing nickel oxide.

[Claim 9] Micro-wiring comprising the composite fine structure according to any one of claims 1 to 7,
the micro-wiring further comprising: a linear micro-wire portion having a cross sectional diameter of 100 μm or less; and a coating portion that coats the surface of the micro-wire portion,
wherein the micro-wire portion is constituted from the metal portion containing copper, and
the coating portion is constituted from the metal oxide portion containing copper oxide.

[Claim 10] A temperature sensor comprising the composite fine structure according to any one of claims 1 to 7,
the temperature sensor further comprising: a sensor portion; and an edge part formed at the periphery of the sensor portion,
wherein the sensor portion is constituted from the metal portion containing copper and copper (I) oxide, and
the edge part is constituted from the metal oxide portion containing copper (II) oxide.

[Claim 11] An article comprising the composite fine structure according to any one of claims 1 to 7.

[Claim 12] A method for producing a composite fine structure, comprising:
preparing a metal oxide nanoparticle-containing liquid, which contains metal oxide nanoparticles and a laser-curable resin that is cured by being irradiated with laser light;
supplying the metal oxide nanoparticle-containing liquid to a surface of a base material; and
irradiating the metal oxide nanoparticle-containing liquid supplied to the surface of the base material, with an ultrashort pulse laser,
wherein a composite fine structure is formed by the irradiation with the ultrashort pulse laser, the composite fine structure containing: a metal oxide portion containing a resin portion in which the laser-curable resin is cured, and the metal oxide nanoparticles; and a metal portion in which the metal oxide nanoparticles are reduced and bonded to each other, the dimension of at least one of the metal oxide portion and the metal portion being 100 μm or less.

[Claim 13] The method according to claim 12, wherein the metal oxide

nanoparticles contain at least one type of oxide selected from the group consisting of oxides of gold (Au), silver (Ag), copper (Cu), nickel (Ni), iron (Fe) and titanium (Ti).

[Claim 14]

An additive manufacturing apparatus for manufacturing a three-dimensional article having a metal oxide portion containing metal oxide nanoparticles, and a metal portion in which at least some of the metal oxide nanoparticles are reduced and directly bonded to each other, the dimension of at least one of the metal oxide portion and the metal portion being 100 μm or less,

the additive manufacturing apparatus comprising:

a laser oscillation device that generates an ultrashort pulse laser irradiated to a metal oxide nanoparticle-containing liquid containing the metal oxide nanoparticles and a laser-curable resin that is cured by being irradiated with laser light; and

a control device that controls laser irradiation position and laser oscillation conditions for the laser oscillation device, wherein

the control device includes:

a first storage unit that stores image data corresponding to a cross-section shape of a three-dimensional article to be manufactured and including at least positional information of a site constituted from the metal portion (A) in the cross-section;

a second storage unit that stores at least previously acquired laser irradiation conditions for forming the metal portion (A) by reducing the metal oxide nanoparticles; and

a laser oscillation conditions setting unit configured or programmed to set a position corresponding the cross-section in the metal oxide nanoparticle-containing liquid as the laser irradiation position based on the image data and to set laser oscillation conditions of a position corresponding the site constituted from the metal portion (A) as the laser irradiation conditions for forming the metal portion (A).

[Claim 15]

The apparatus according to claim 14, wherein

the image data further includes a positional information of a site constituted from the metal oxide portion (B),

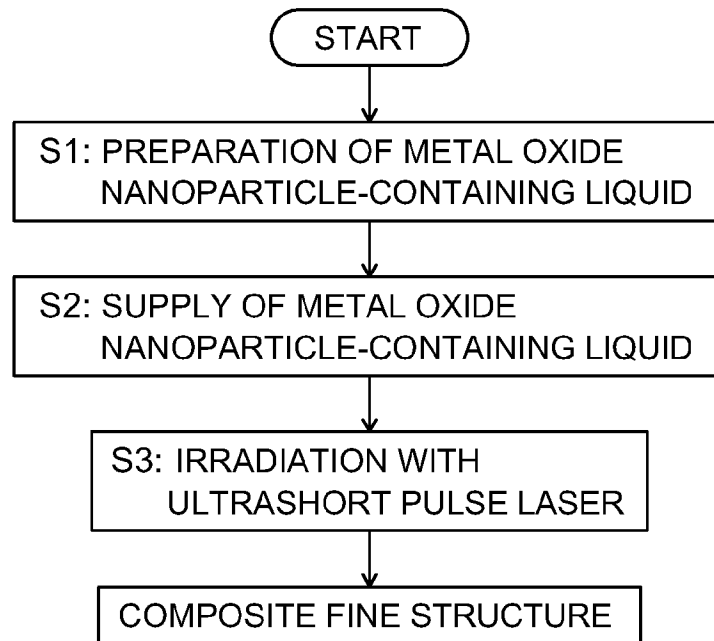
the second storage unit stores laser irradiation conditions for forming the metal oxide portion (B) by curing a laser-curable resin without reducing the metal oxide nanoparticles, and

a laser oscillation conditions setting unit configured or programmed to set laser oscillation conditions of a position corresponding the site con-

stituted from the metal portion (B) as the laser irradiation conditions for forming the metal portion (B).

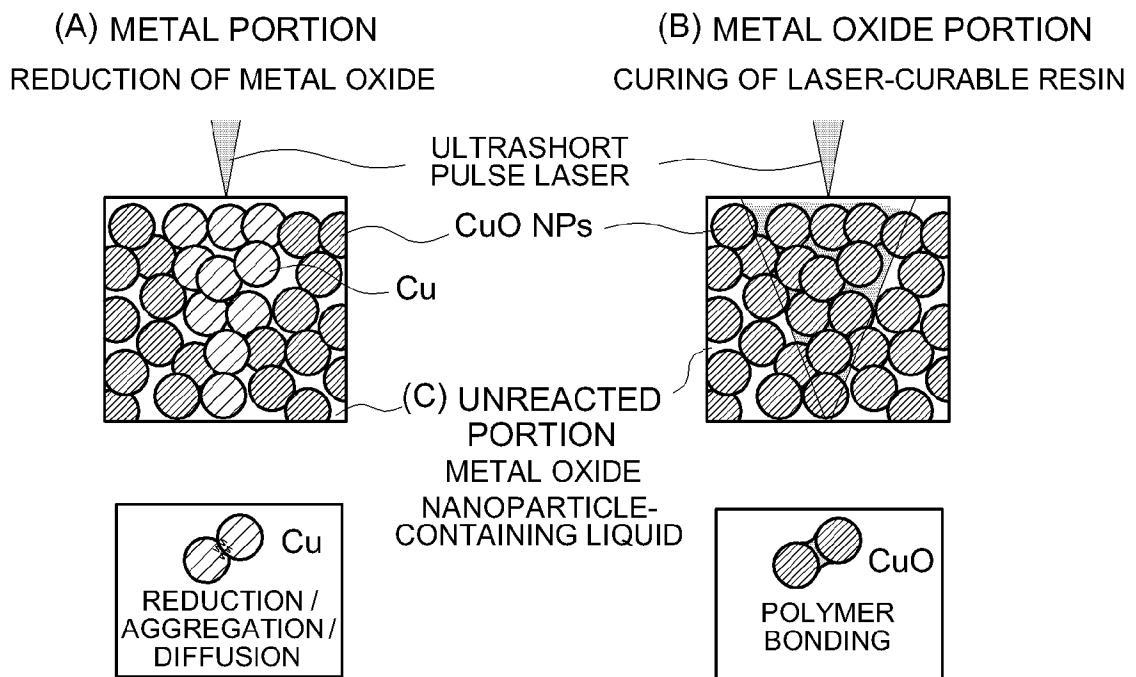
[Fig. 1]

FIG.1



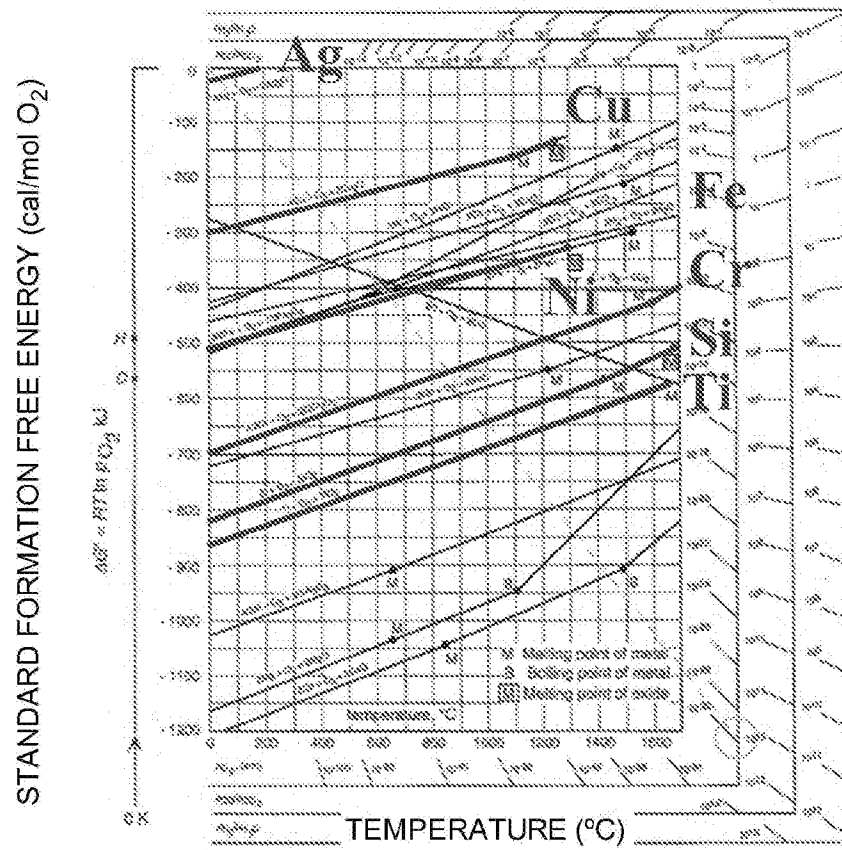
[Fig. 2]

FIG.2



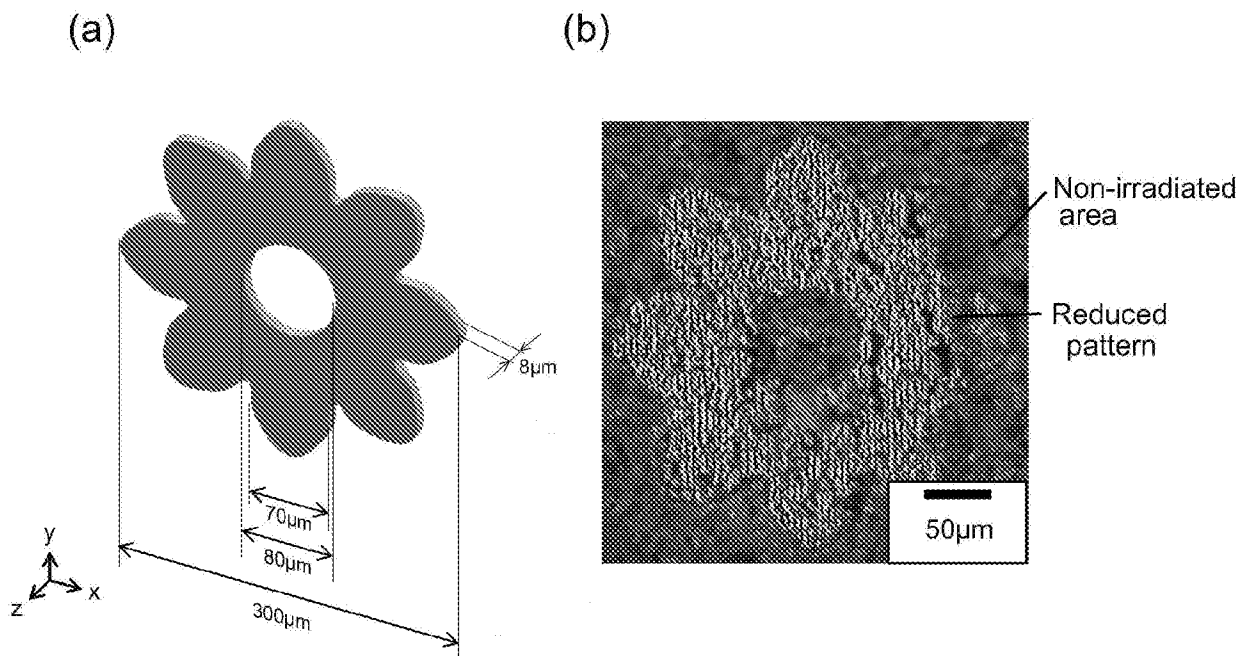
[Fig. 3]

FIG.3

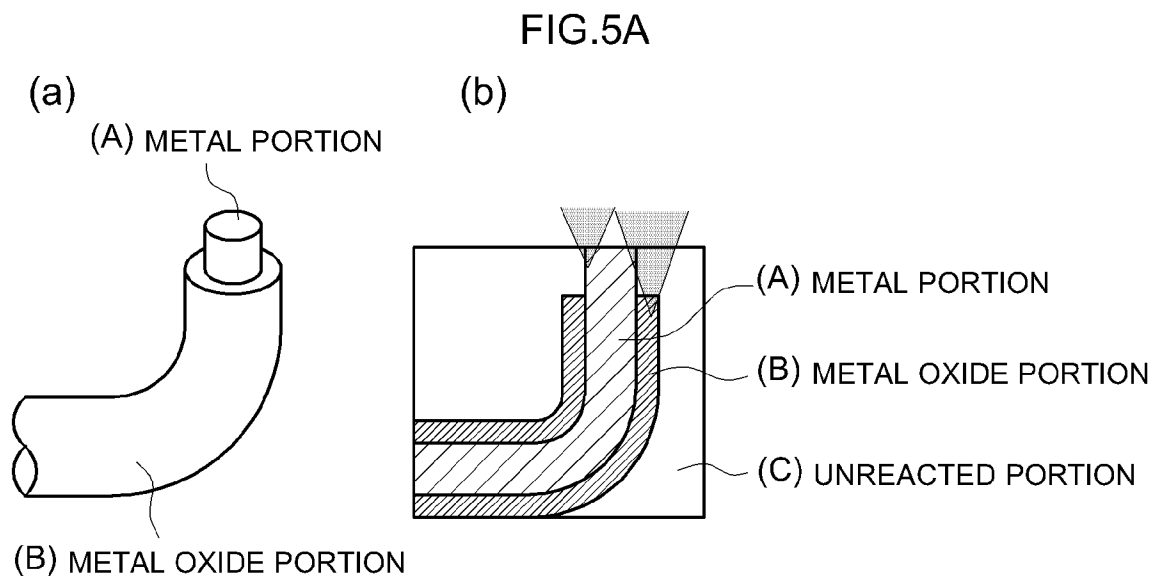


[Fig. 4]

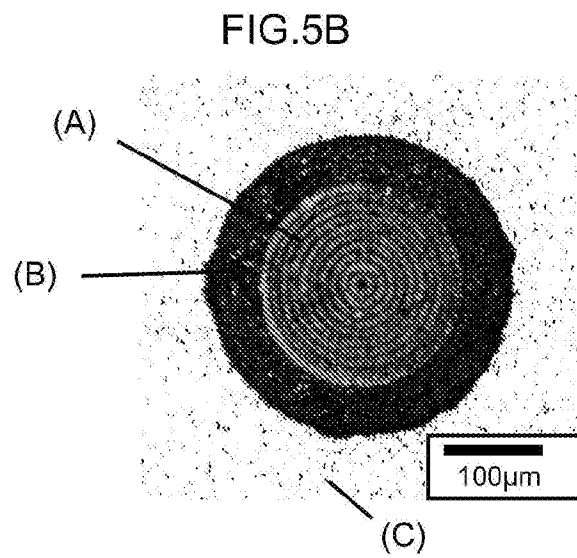
FIG.4



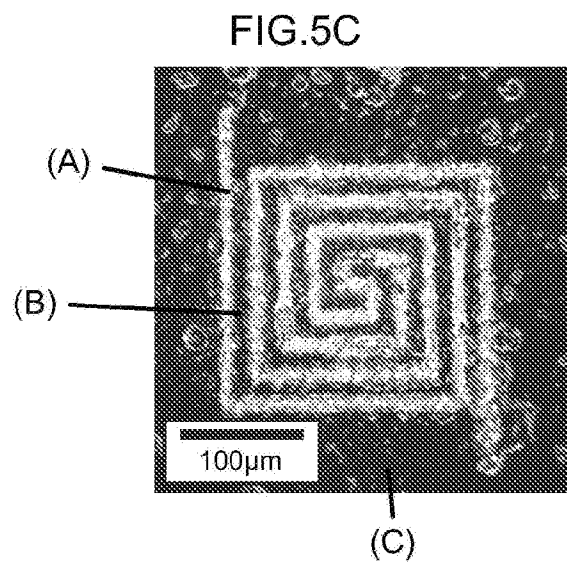
[Fig. 5A]



[Fig. 5B]

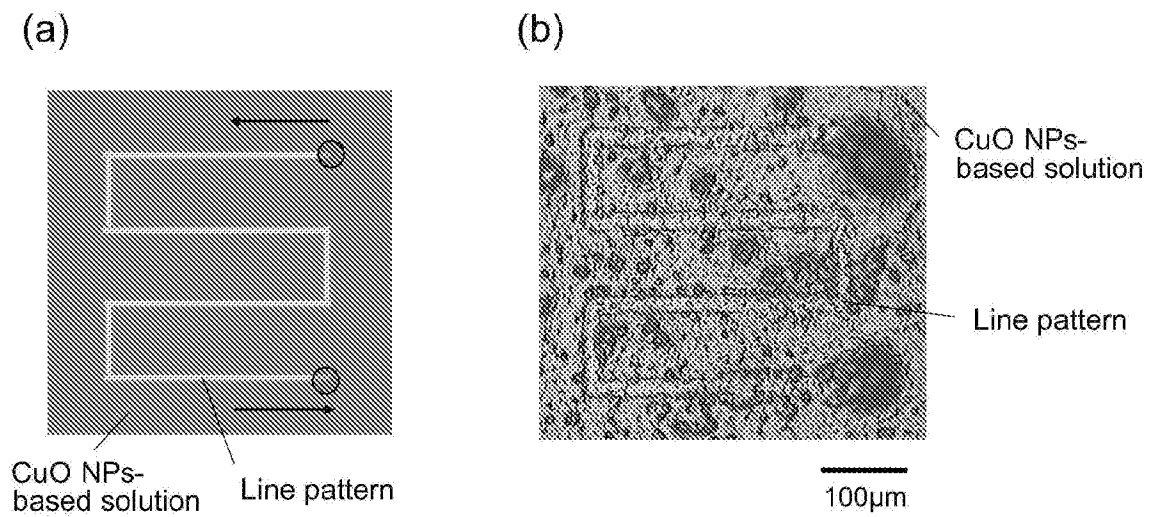


[Fig. 5C]



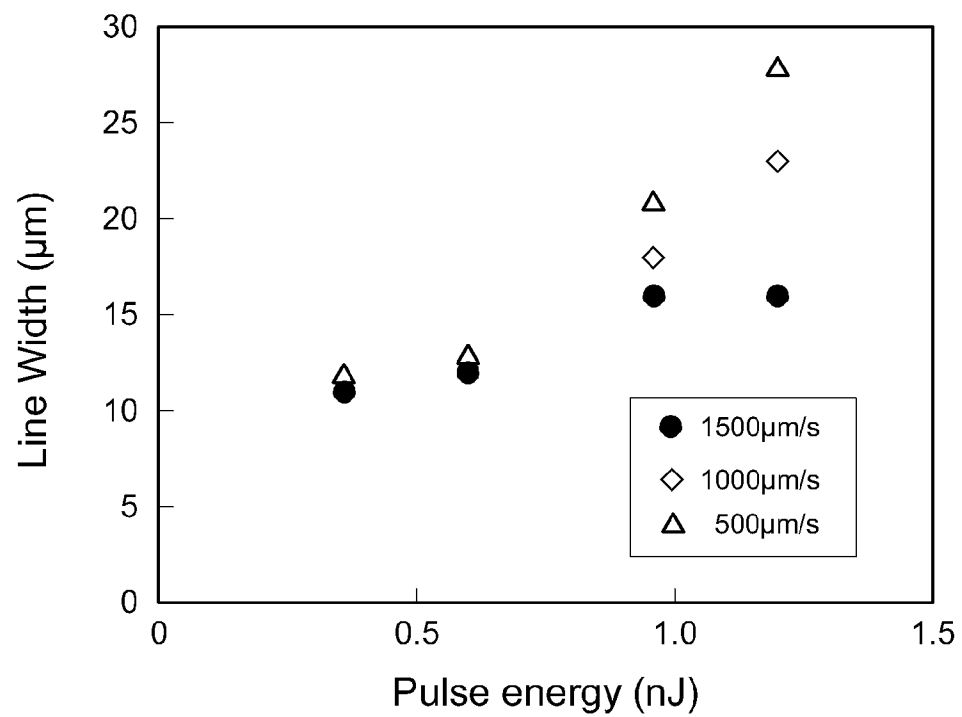
[Fig. 6]

FIG.6



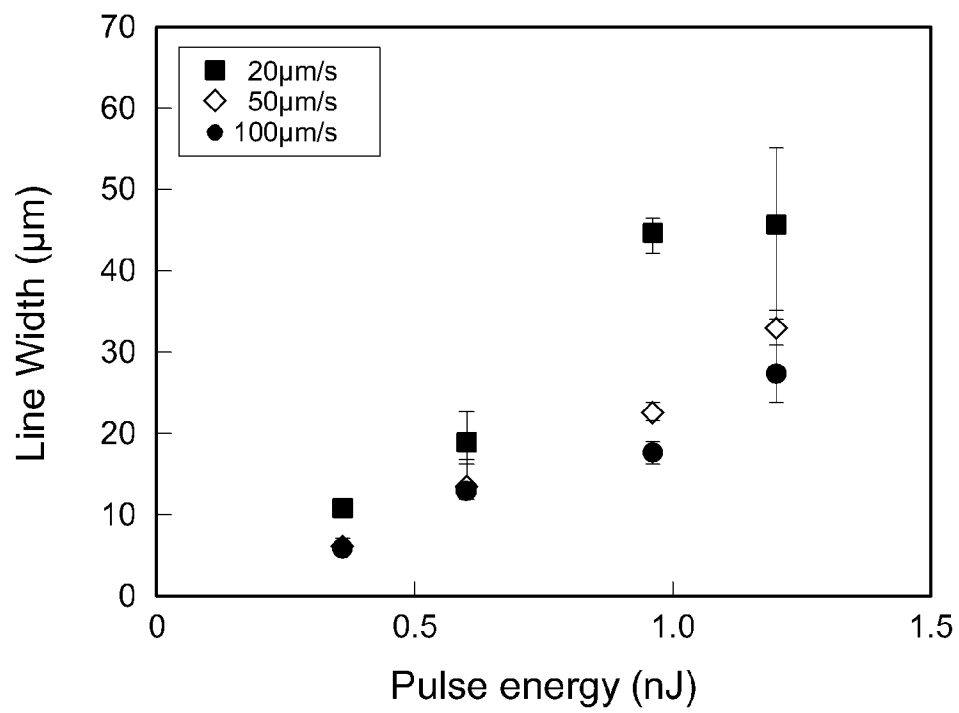
[Fig. 7]

FIG.7



[Fig. 8]

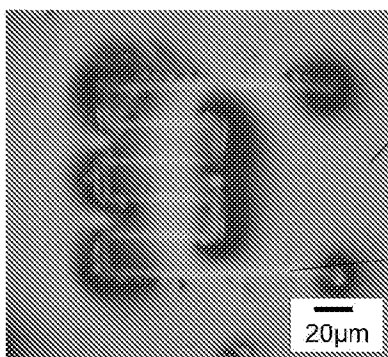
FIG.8



[Fig. 9]

FIG.9

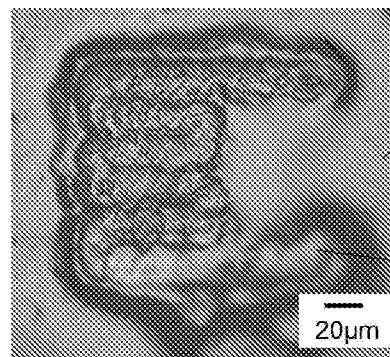
(a)

CuO NPs-
based solution

Line pattern

20 μm

(b)

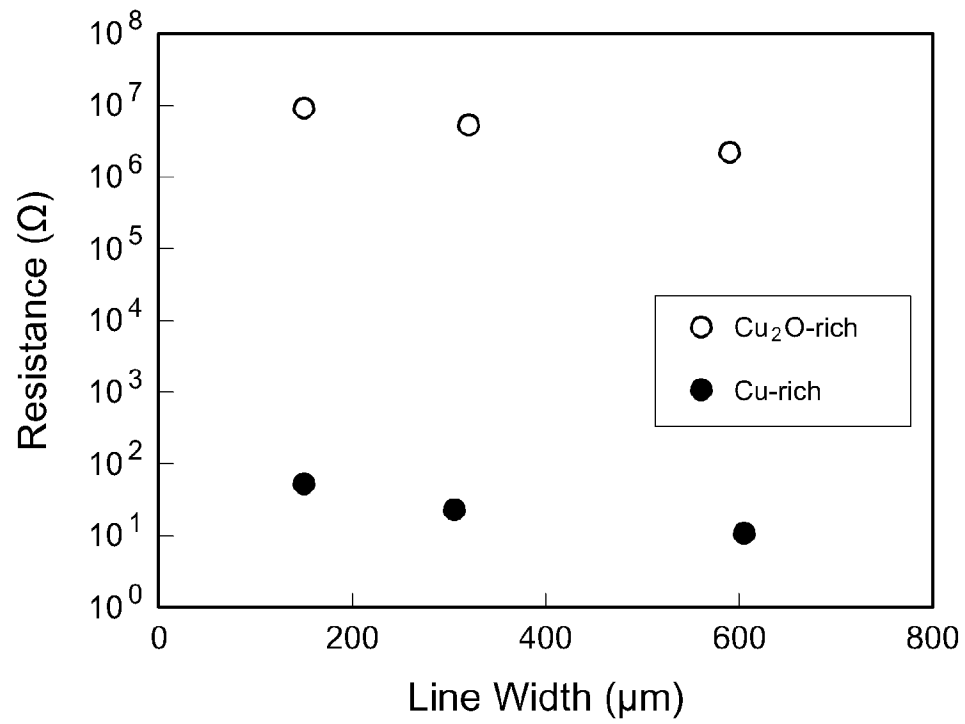
CuO NPs-
based solution

Line pattern

20 μm

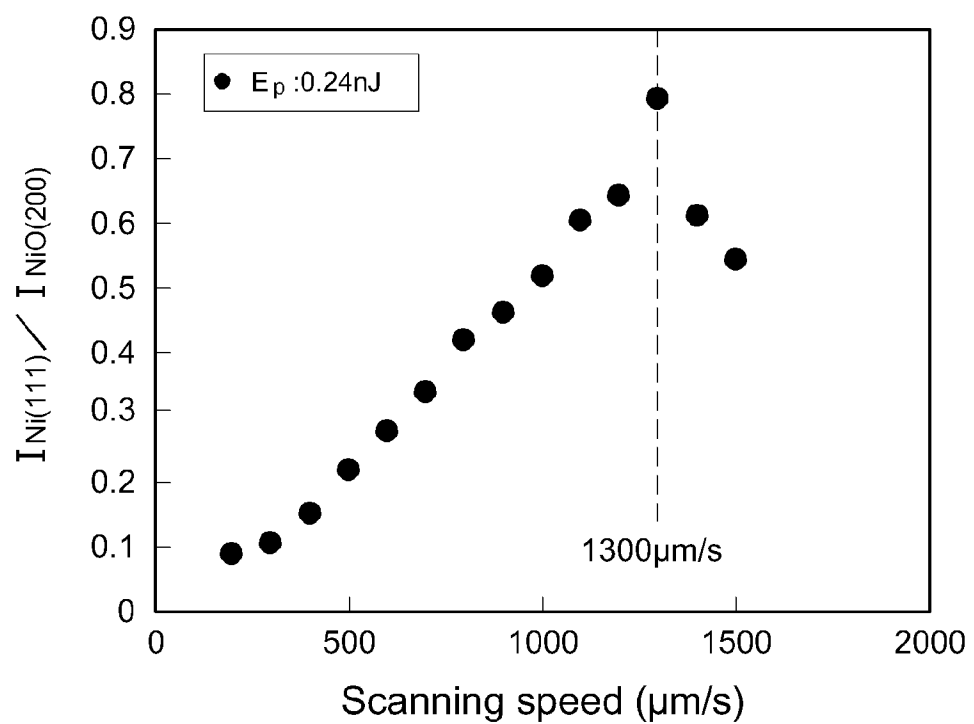
[Fig. 10]

FIG.10



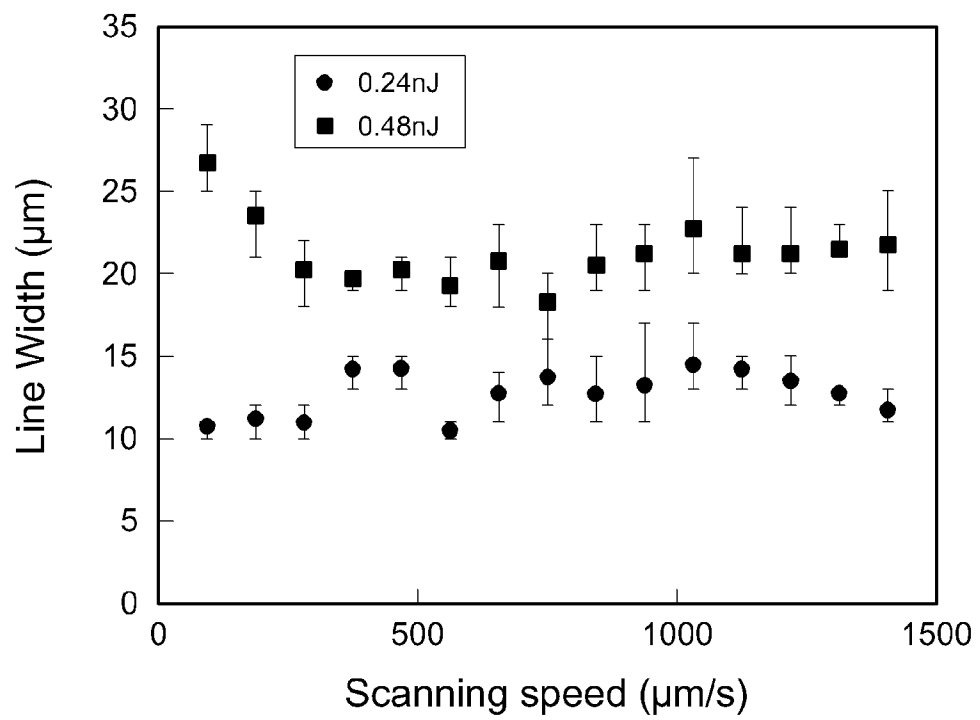
[Fig. 11]

FIG.11



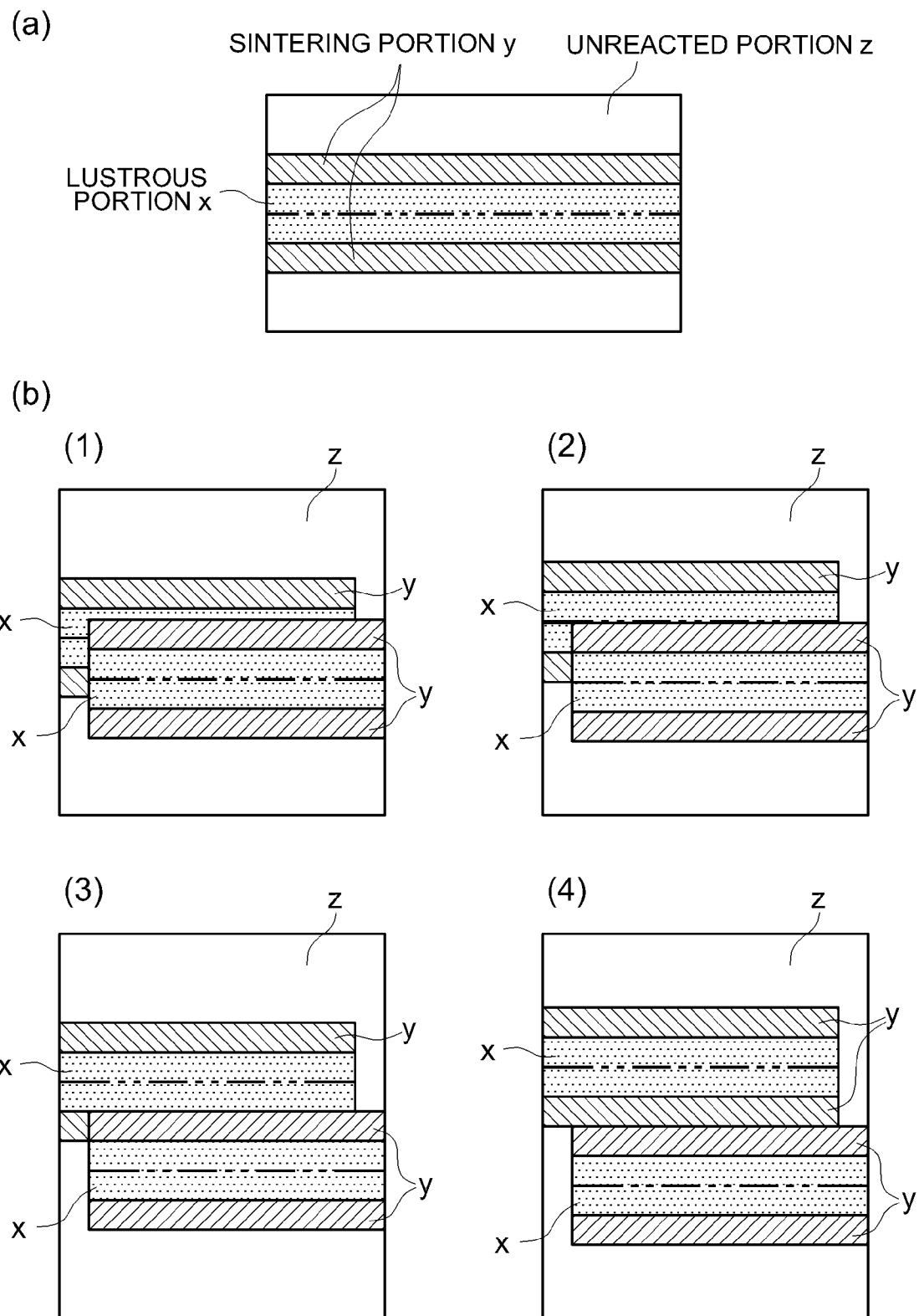
[Fig. 12]

FIG.12



[Fig. 13]

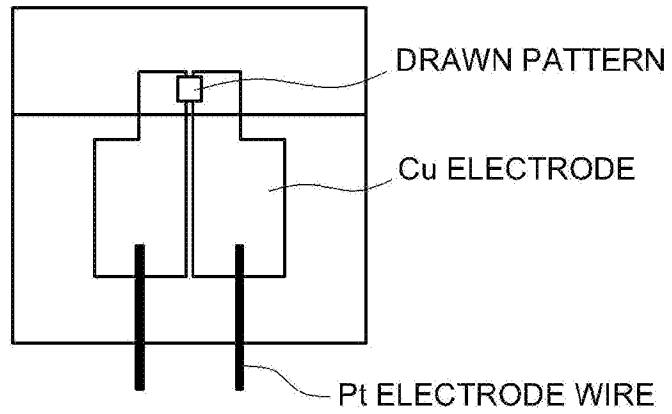
FIG.13



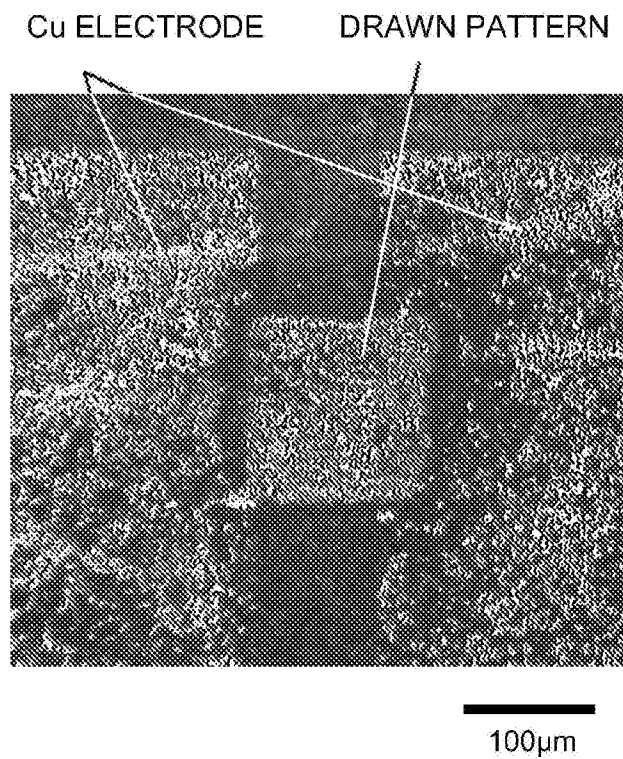
[Fig. 14]

FIG.14

(a)



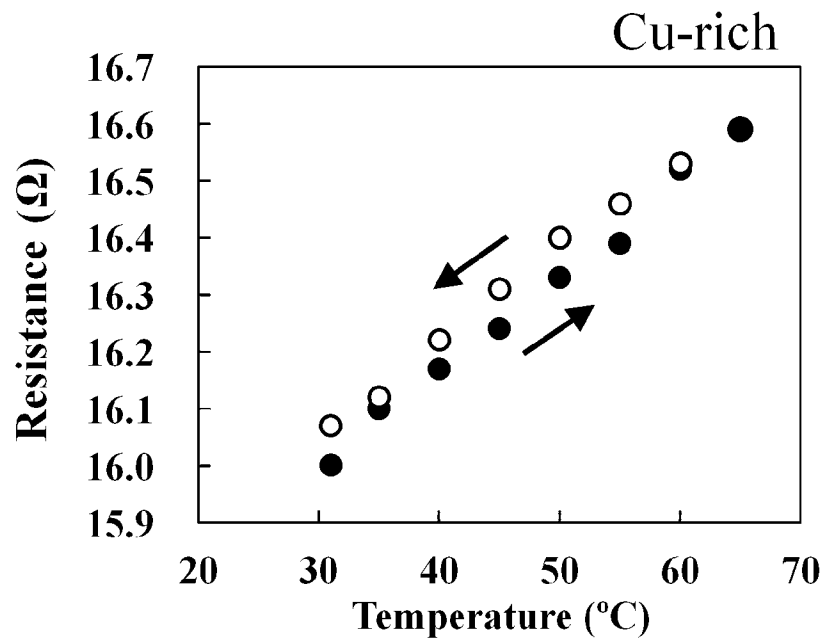
(b)



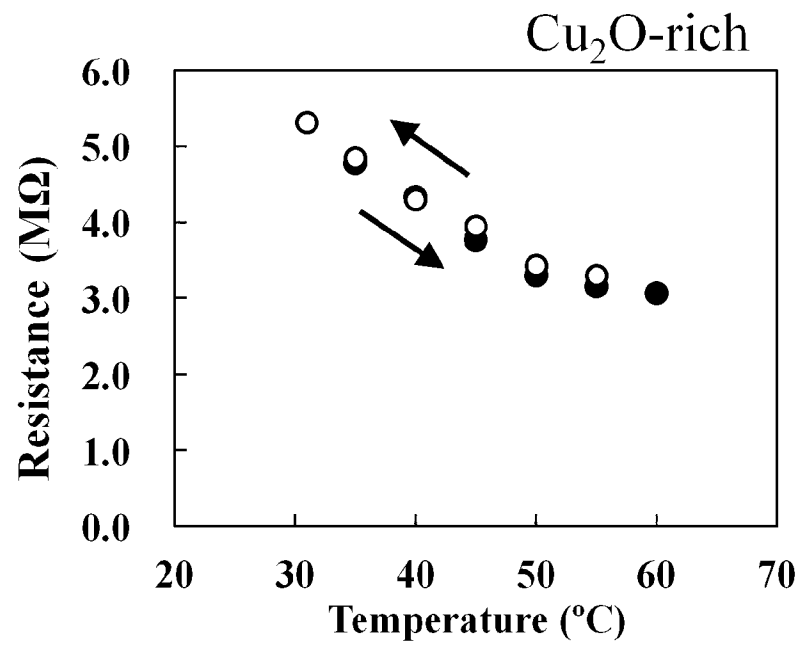
[Fig. 15]

FIG.15

(a)

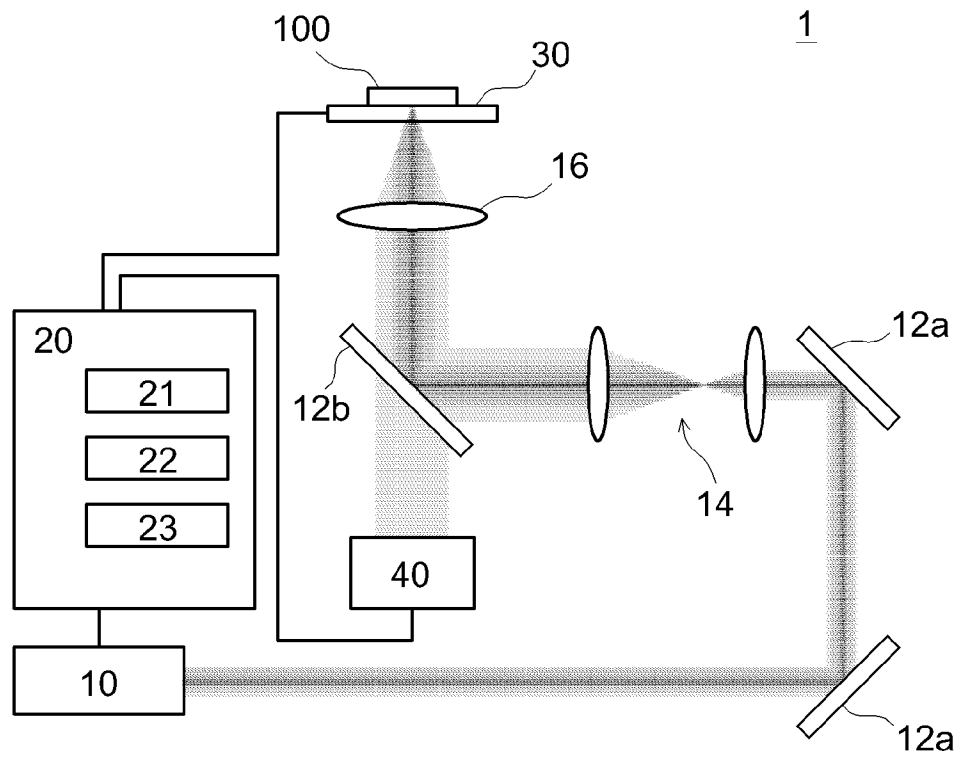


(b)



[Fig. 16]

FIG.16



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/000944

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. See extra sheet		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int.Cl. B29C67/00, B22F3/105, B22F3/16, B81B5/00, B81C1/00, B82Y30/00, B82Y40/00, G01K7/16, G03F7/033, H01L21/027,		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2016 Registered utility model specifications of Japan 1996-2016 Published registered utility model applications of Japan 1994-2016		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P.X P.A	KENKI Tamura, MIZUE Mizoshiri, JUNPEI Sakurai, SEIICHI Hata, Patterning properties of nickel microstructures using femtosecond laser induced reduction, LAMP 2015, the 7th International Congress on Laser Advanced Materials Processing, Congress Program & Technical Digest, page 271, 2015.05.26	1-13 14-15
P.X P.A	KENKI Tamura et al., Patterning properties of nickel microstructure using femtosecond laser induced reduction, Proceedings of LAMP2015-the 7th International Congress on Laser Advanced Materials Processing, page 1-4, 2015.08.24 http://www.jlps.gr.jp/en/proc/lamp/15/A034_Tamura_et_al.pdf	1-13 14-15
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
11.05.2016		24.05.2016
Name and mailing address of the ISA/JP		Authorized officer
Japan Patent Office		Takuya IMAI
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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P.X P.A	KENKI Tamura et al., LAMP2015, The 7th international Congress on Laser Advanced Materials Processing, 2015.05.27 http://www.jlps.gr.jp/lamp/lamp2015	1-13 14-15
P.X P.A	MIZUE Mizoshiri, SHUN Arakane, JUNPEI Sakurai, SEIICHI Hata, Reduction of CuO nanoparticles for Cu micropatterning by femtosecond laser pulses, LAMP2015, The 7th International Congress on Laser Advanced Materials Processing, Congress Program & Technial Digest, page252, 2015.05.26	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., Reduction of CuO nanoparticles for Cu micropatterning by femtosecond laser pulses, Proceeding of LAMP2015-the 7th International Congress on Laser Advanced Materials Processing, page1-4, 2015.08.04 http://www.jlps.gr.jp/en/proc/lamp/15/A126 Mizushiri et al.pdf	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., LAMP2015, The 7th international Congress on Laser Advanced Materials Processing, 2015.05.29	1-13 14-15
P.X P.A	MIZUE Mizoshiri SHUN Arakane, JUNPEI Sakurai, SEIICHI Hata, Fabrication of micro temperature sensor using direct femtosecond laser reduction patterning, Proceedings of the 83rd Laser Materials Processing Conference, page179, 2015.06.11	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., Proceedings of the 83rd Laser Materials Processing Conference, 2015.07.17 http://218.228.197.42/cgi-bin/cbdb/db.exe?page=DB View&did=16	1-13 14-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/000944

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P.X P.A	MIZUE Mizoshiri et al., Proceedings of the 83rd Laser Materials Processing Conference, 2015.06.11, http://www.jlps.gr.jp/news/2015/07/83.html	1-13 14-15
P.X P.A	MIZUE Mizoshiri, KENKI Tamura, JUNPEI Sakurai, SEIICHI Hata, Reduction Properties of Nickel Microstructures Fabricated by Direct Femtosecond Laser Reduction Patterning, 2015 JSME-IIP /ASME-ISPS Joint Conference on Micromechatronics for Information and Precision Equipment (MIPE2015), 2015.06.14	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., 2015JSME-IIP/ASME-ISPS Joint Conference on Micromechatronics for Information and Precision Equipment (MIPE2015), 2015.06.15	1-13 14-15
P.X P.A	MIZUE Mizoshiri, YASUAKI Ito, SHUN Arakane, JUNPEI Sakurai, SEIICHI Hata, Direct writing of micro-thermoelectric sensors using femtosecond laser reduction, Expanded Abstracts (The 76th Autumn Meeting 2015), 03-078, The Japan Society of Applied Physics and Related Societies, 2015.08.31	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., Expanded Abstracts (The 76th Autumn Meeting 2015), 2015.08.31 https://confit.atlas.jp/guide/event/jsap2015a/subject/13p-2F-7/tables?cryptoID	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., Expanded Abstracts (the 76th Autumn Meeting 2015), 2015.09.13 http://confit.atlas.jp/guide/event/jsap2015a/notifications	1-13 14-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/000944

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P.X P.A	SHUN Arakane, MIZUE Mizoshiri, JUNPEI Sakurai, SEIICHI Hata, Electrical conductivity of Cu micropatterns fabricated by direct femtosecond laser reduction, Mechanical Engineering Congress, 2015 Japan (MECJ-15), S0440102, 2015.09.13	1-13 14-15
P.X P.A	SHUN Arakane et al., Mechanical Engineering Congress, 2015 Japan (MECJ-15), 2015.09.14	1-13 14-15
P.X P.A	KENKI Tamura, MIZUE Mizoshiri, JUNPEI Sakurai, SEIICHI Hata, Patterning of Ni microstructures by femtosecond laser reduction of NiO Nanoparticles, Mechanical Engineering Congress, 2015 Japan (MECJ-15), S0440103, 2015.09.13	1-13 14-15
P.X P.A	KENKI Tamura et al., Mechanical Engineering Congress, 2015 Japan (MECJ-15), 2015.09.14	1-13 14-15
P.X P.A	MIZUE Mizoshiri, KENKI Tamura, SHUN Arakane, YASUAKI Ito, JUNPEI Sakurai, SEIICHI Hata, Femtosecond laser direct fabrication of metal microstructures, Reports on the 481st Topical Meeting of the Laser Society of Japan, Laser Processing for the Next Jeneration, RTM-15-32-36, 2015.09.29	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., Reports on the 481st Topical Meeting of the Laser Society of Japan, Laser Processing for the Next Jeneration, 2015.09.29	1-13 14-15
P.X P.A	YASUAKI Ito, MIZUE Mizoshiri, SHUN Arakane, JUNPEI Sakurai, SEIICHI Hata, Fabrication of Cu ₂ O-rich micro-temperature sensor using direct femtosecond laser reduction patterning, Proceeding of the 7th micro-nano engineering symposium, 29pm1-B-4, 2015.10.29	1-13 14-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/000944

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P.X P.A	YASUAKI Ito et al., Proceeding of the 7th micro-nano engineering symposium, 2015.10.21 https://www.semiconductorportal.com/submission2014/dl.cfm	1-13 14-15
P.X P.A	MIZUE Mizoshiri, YASUAKI Ito, SHUN Arakane, JUNPEI Sakurai, SEIICHI Hata, Direct Fabrication of micro-temperature sensor using femtosecond laser reduction patterning, Digest of the 28th International Microprocesses and Nanotechnology conference:MNC2015, 12P-7-108, 2015.11.10	1-13 14-15
P.X P.A	MIZUE mizoshiri et al., the 28th International Microprocesses and Nanotechnology conference:MNC2015, 2015.11.12, http://imnc.jp/japanese2015html	1-13 14-15
P.X P.A	SHUN Arakane, MIZUE Mizoshiri, JUNPEI Sakurai, SEIICHI Hata, Resistance temperature characteristics of Cu-based micropatterns fabricated using femtosecond laser reduction patterning, Expanded Abstracts of the 1st innovation from JSME2015, page54, 2015.11.14	1-13 14-15
P.X P.A	SHUN Arakane et al., the 1st innovation from JSME2015, 2015.11.11 http://mnp.mech.nagoya-u.ac.jp/pub/iJSME_Proceedings_PW.pdf	1-13 14-15
P.X P.A	SHUN Arakane et al., the 1st innovation from JSME2015, 2015.11.14 http://innovation-conf.com/participant/	1-13 14-15
P.X P.A	MIZUE Mizoshiri, YASUAKI Itou, JUNPEI Sakurai, SEIICHI Hata, Microtemperature sensor fabricated using femtosecond laser pulse induced reduction, Expanded Abstracts of the 1st innovation from JSME2015, page68, 2015.11.14	1-13 14-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/000944

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P.X P.A	MIZUE Mizoshiri et al., the 1st innovation from JSME2015, 2015.11.11	1-13 14-15
P.X P.A	MIZUE Mizoshiri et al., the 1st innovation from JSME2015, 2015.11.14 http://innovation-conf.com/participant/	1-13 14-15
P.X P.A	KENKI Tamura, MIZUE Mizoshiri, JUNPEI Sakurai, SEIICHI Hata, Micropatterning properties using femtosecond laser reduction of nickel oxide nanoparticles, Expanded Abstracts of the 1st innovation from JSME2015, page18, 2015.11.14	1-13 14-15
P.X P.A	KENKI Tamura et al., The 1st innovation from JSME2015, 2015.11.11 http://mnp.mech.nagoya-u.ac.jp/pub/iJSME_Proceedings_PW.pdf	1-13 14-15
P.X P.A	KENKI Tamura et al., the 1st innovation from JSME2015, 2015.11.15 http://innovation-conf.com/participant/	1-13 14-15
P.X P.A	SEIICHI Hata, JUNPEI Sakurai, MIZUE Mizoshiri, MEMS and Micromachining Laboratory, Nagoya University, Expanded abstracts of the 1st innovation from JSME2015, page66, 2015.11.14	1-13 14-15
P.X P.A	SEIICHI Hata et al., the 1st innovation from JSME2015, 2015.11.11 http://mnp.mech.nagoya-u.ac.jp/pub/iJSME_Proceedings_PW.pdf	1-13 14-15
P.X P.A	SEIICHI Hata et al., the 1st innovation from JSME2015, 2015.11.14 http://innovation-conf.com/participant/	1-13 14-15
P.X P.A	NanotechJapan, 2015.08.25 http://nanonet.mext.go.jp/topics_insti/?mode=article_no=2921	1-13 14-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/000944

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2014-116315 A (Applied Nanotech Holdings, Inc.,) 2014.06.26, claims, [0070]-[0091] & US 2008/0286488 A1 claims, [0095]-[0115] & EP 2414109 A	1-2, 4, 6, 9, 11 3, 5, 7-8, 10, 12-15
X A	JP 2003-92383 A (Hitachi, Ltd.) 2003.03.28, claims, [0027]-[0035] (No Family)	1-2, 6, 11 3-5, 7-10, 12-15
X A	JP 2014-167872 A (Fujifilm Corporation) 2014.09.11, claims, [0037],[0040], [0050]-[0069] (No Family)	1-7, 9, 11-13 8, 10, 14-15
X A	KENKI Tamura et al., Patterning properties of nickel microstructures using femtosecond laser direct reduction, Expanded Abstracts of the 62nd Spring Meeting 2015, page648, The Japan Society of Applied Physics and Related Societies, 2015.02.26	1-8, 11-13 9-10, 14-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/000944

CLASSIFICATION OF SUBJECT MATTER

B29C67/00(2006.01)i, B22F3/105(2006.01)i, B22F3/16(2006.01)i,
B81B5/00(2006.01)i, B81C1/00(2006.01)i, B82Y30/00(2011.01)i,
B82Y40/00(2011.01)i, G01K7/16(2006.01)i, G03F7/033(2006.01)i,
H01L21/027(2006.01)i, B33Y10/00(2015.01)n, B33Y30/00(2015.01)n,
B33Y80/00(2015.01)n