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(54) **METHOD FOR MODIFYING NICKEL POWDER AND METHOD FOR PRODUCING SAME**

(57) The purpose of the present invention is to provide a method for modifying nickel microparticles weight loss of which occurs due to heat treatment such as burning and a method for producing nickel microparticles comprising the modification method.

Provided is a method for modifying nickel microparticles comprising a step of making an acid and/or hydrogen peroxide act on nickel microparticles weight loss of which occurs due to heat treatment such as burning and

a method for producing nickel microparticles comprising the modification method. The step of making an acid and/or hydrogen peroxide act reduces a rate of weight loss due to heat treatment of the nickel microparticles, nitric acid or a mixture of acids that include nitric acid is preferably used as the acid, and the nickel microparticles and acid and/or hydrogen peroxide are preferably made to act in a ketonic solvent.

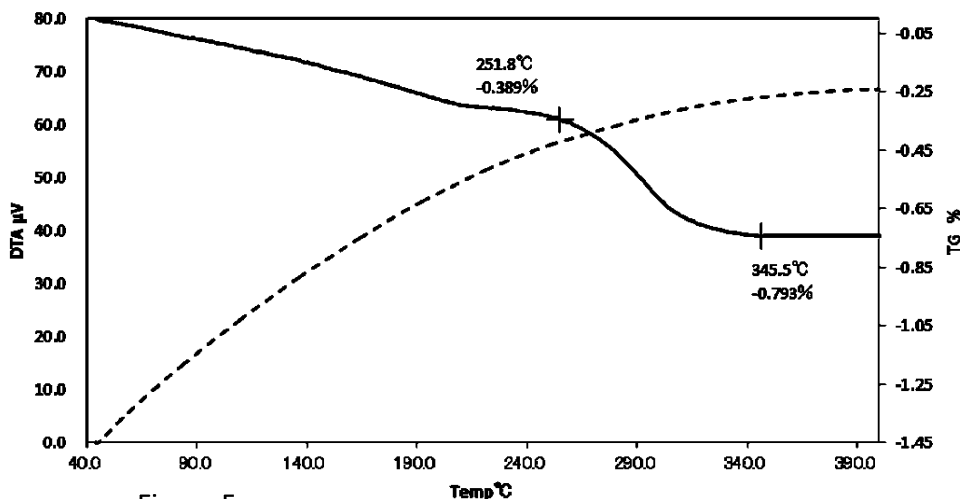


Figure 5

Description

Technical Field

[0001] The present invention relates to a method for modifying nickel microparticles and a method for producing nickel microparticles.

[0002] Nickel microparticles, which are a widely used material as an electrically conductive material including a laminated ceramic condenser and a substrate thereof, as well as an electrode material, have been used as ones controlled in crystallite diameter and particle diameter and particle size distribution according to purpose.

[0003] The methods for producing nickel microparticles include a method using a gas phase method as known in Patent Document 1 and a method using a liquid phase method as known in Patent Document 2.

[0004] Generally, with nickel microparticles obtained using these methods, a few percent of weight loss is often confirmed in a simultaneous TG-DTA (Thermogravimetry-Differential Thermal Analysis) measurement, and which contributes to a defect such as cracking that occurs, for example, during burning when a laminated ceramic condenser is produced using slurry of nickel microparticles for an internal electrode.

[0005] In addition, such nickel microparticles also have a problem in storage stability, and also often form nickel hydroxide in a few days to a few weeks when stored under an air atmosphere, and there has been a problem such that use of nickel microparticles becomes difficult in that case.

[0006] The following conventional arts propose solutions to the above problems. For example, a method where hydrogen reduction processing using hydrogen gas is performed after oxidizing nickel powder to some degree is proposed in Patent Document 3, and a method where nickel powder is added into and dispersed in an aqueous solution containing a water-soluble fatty acid salt, the aqueous solution slurry is adjusted from acidic to neutral pH, the nickel powder is filtered out from the aqueous solution slurry, the nickel powder thus obtained is heat-treated, then a solvent slurry, prepared by mixing a solvent, a fatty acid, and the nickel powder, is heated and stirred to volatilize the solvent, and thereafter the nickel powder obtained is heat-treated is proposed in Patent Document 4. A method where nickel microparticles having a nickel hydroxide coating are processed by a plasma of oxygen-containing gas generated by glow discharge to form a coating of nickel oxide is proposed in Patent Document 5.

[0007] However, the method of Patent Document 3 has such problems as requiring explosion-proof measures for facilities and involving danger in the production of microparticles due to the use of hydrogen gas. Also, the method of Patent Document 4 has such problems that the process becomes extremely complex, productivity is still low, it is difficult to remove the fatty acid salt absorbed to the nickel microparticle surfaces, and heat treatment is required. Further, with Patent Document 5, there are such problems as requiring high energy and an expensive apparatus for processing by the plasma of the oxygen-containing gas. Thus in regard to the issues described above, the conventional arts not only have difficulties in reducing the weight loss rate in the simultaneous TG-DTA measurement but also do not provide an industrially inexpensive simple solution suited for mass production.

[0008] On the other hand, up to now, Applicant of the presently applied invention has proposed the methods for producing nickel microparticles described in Patent Document 6 and Patent Document 7. Patent Document 6 relates to a method of separating nickel microparticles in a thin film fluid formed between processing surfaces which are able to approach and separate from each other and rotate relative to each other. In Patent Document 7, there is described a method for making nickel microparticles have a sharper particle diameter distribution, a method for controlling particle diameter, and a method for controlling crystallite diameter. By the methods described in Patent Document 6 and Patent Document 7, it is possible to mass-produce nickel microparticles of uniform particle size distribution extremely simply.

[0009] Even in terms of the nickel microparticles prepared using the production methods described in Patent Document 6 and Patent Document 7, however, there is no disclosure of a method for producing nickel microparticles reduced in weight loss rate in simultaneous TG-DTA measurement, and the defect such as cracking in the burning process cannot be solved when a laminated ceramic condenser is produced.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0010]

Patent Document 1: Japanese Patent Laid-Open Publication No. 2014-189820

Patent Document 2: Japanese Patent Laid-Open Publication No. 2014-162967

Patent Document 3: Japanese Patent Laid-Open Publication No. 2001-073001

Patent Document 4: Japanese Patent Laid-Open Publication No. 2003-129105

Patent Document 5: Japanese Patent Laid-Open Publication No. 2014-173105

Summary of the Invention

Problems to be Solved by the Invention

[0011] In light of such circumstances, the present invention provides a method for modifying nickel microparticles with a reduced weight loss rate in simultaneous TG-DTA measurement and a method for producing nickel microparticles comprising this method for modifying nickel microparticles.

[0012] As a result of an intensive examination carried out in order to solve the abovementioned problems, the inventor of the presently applied invention have found that the abovementioned object can be achieved by a method for modifying nickel microparticles to be described hereinafter and a method for producing nickel microparticles comprising this method for modifying nickel microparticles and thereby could accomplish the presently applied invention.

Means for Solving the Problems

[0013] Specifically, the present invention relates to a method for modifying nickel microparticles comprising a step of making an acid and/or hydrogen peroxide act on nickel microparticles weight loss of which occurs due to heat treatment such as burning.

[0014] The present invention relates to a method for modifying nickel microparticles, wherein the step of making an acid and/or hydrogen peroxide act reduces a rate of weight loss due to heat treatment of the nickel microparticles.

[0015] In addition, the present invention may be executed as an embodiment wherein the rate of weight loss due to heat treatment of the nickel microparticles is a weight loss rate in simultaneous thermogravimetry-differential thermal analysis measurement, and the weight loss rate in a simultaneous thermogravimetry-differential thermal analysis measurement under a nitrogen atmosphere of the nickel microparticles is 1% or less in a range of 40°C to 400°C.

[0016] Further, the present invention relates to a method for modifying nickel microparticles, wherein nitric acid or a mixture of acids that include nitric acid is used as the acid.

[0017] The present invention relates to a method for modifying nickel microparticles, wherein the nickel microparticles and acid and/or hydrogen peroxide are made to act in a ketonic solvent.

[0018] The present invention relates to a method for modifying nickel microparticles, wherein a molar ratio of the acid to the nickel microparticles is in a range of 0.001 to 0.1.

[0019] The present invention relates to a method for modifying nickel microparticles, wherein a molar ratio of the hydrogen peroxide to the nickel microparticles is in a range of 0.001 to 2.0.

[0020] The present invention relates to a method for modifying nickel microparticles, wherein the step of making an acid and/or hydrogen peroxide act includes an ultrasonic processing, a stirring processing, or a microwave processing.

[0021] In addition, the present invention may be executed as an embodiment wherein the stirring processing is performed using a stirrer provided with a rotating stirring blade.

[0022] The present invention relates to a method for modifying nickel microparticles, wherein powder of the nickel microparticles on which the acid and/or hydrogen peroxide was made to act is stored under an air atmosphere.

[0023] The present invention relates to a method for modifying nickel microparticles, wherein the nickel microparticles are nickel microparticles separated by a microreactor which makes at least two kinds of fluids to be processed react.

[0024] The present invention relates to a method for modifying nickel microparticles comprising a step of making a substance which reacts with nickel hydroxide act on nickel microparticles on at least surfaces of which nickel hydroxide is present to reduce the nickel hydroxide.

[0025] The present invention relates to a method for producing nickel microparticles comprising a method for modifying nickel microparticles described above.

[0026] Further, the present invention relates to a method for producing nickel microparticles, being a method for producing the nickel microparticles using a microreactor, the said microreactor comprising a first processing surface and a second processing surface which are disposed facing each other so as to be able to approach and/or separate from each other, at least one of which rotates relative to the other, comprising a step of introducing at least two kinds of fluids to be processed between the first processing surface and the second processing surface, a step of generating a separating force which acts in a direction to separate the first processing surface and the second processing surface from each other by an introducing pressure of the at least two kinds of fluids to be processed imparted to between the first processing surface and the second processing surface, a step of forming a thin film fluid by making the at least two kinds of fluids to be processed converge with each other between the first processing surface and the second processing surface kept at a minute distance and pass through between the first processing surface and the second processing surface while keeping the minute distance between the first processing surface and the second processing surface by

the separating force, and a step of making the fluids to be processed react with each other in the thin film fluid and separating nickel microparticles by the reaction.

Effects of the Invention

[0027] By using the modification method of the present invention, the rate and amount of weight loss in simultaneous TG-DTA measurement of nickel microparticles can be reduced, and the problem of a defect such as cracking in a burning process when, for example, a laminated ceramic condenser is produced using slurry of nickel microparticles for an internal electrode. Moreover, nickel microparticles modified by the modification method of the present invention are excellent in long-term storage stability such as suppressing the formation of nickel hydroxide. Further, when the method for modifying nickel microparticles of the present invention is applied to nickel microparticles produced using a microreactor which makes at least two kinds of fluids to be processed react, a method for producing nickel microparticles comprising the method for modifying nickel microparticles that thoroughly exhibits its performance and is low cost and capable of mass production can be provided.

Brief Description of Drawings

[0028]

[FIG. 1] This is a rough cross-section view of the fluid processing apparatus according to an embodiment of the present invention.

[FIG. 2] This is a rough top view of the first processing surface of the fluid processing apparatus shown in FIG. 1.

[FIG. 3] This is a SEM picture of the nickel microparticle powders obtained in Comparative Example 1 of the present invention.

[FIG. 4] This shows the results of a simultaneous TG-DTA measurement under a nitrogen atmosphere of the nickel microparticles obtained in Comparative Example 1 of the present invention.

[FIG. 5] This shows the results of a simultaneous TG-DTA measurement under a nitrogen atmosphere of the nickel microparticles obtained after acid processing in Example 1 of the present invention.

[FIG. 6] This is a SEM picture of the nickel microparticles obtained by storing for two weeks under an air atmosphere the nickel microparticle powders obtained in Comparative Example 1 of the present invention.

[FIG. 7] This shows the results of a simultaneous TG-DTA measurement under a nitrogen atmosphere of nickel hydroxide.

[FIG. 8] This is a TEM picture of the nickel microparticles obtained in Comparative Example 1 of the present invention.

[FIG. 9] This is a TEM picture of the nickel microparticles obtained after acid processing in Example 1 of the present invention.

[FIG. 10] This is the XRD measurement results of the nickel microparticles in Comparative Example 1 of the present invention.

[FIG. 11] This is an enlarged view of the essential part of the XRD measurement results of the nickel microparticles in Comparative Example 1 of the present invention.

[FIG. 12] FIG. 12 (A) to FIG. 12 (G) are the XRD measurement results of the nickel microparticles obtained after acid processing and/or hydrogen peroxide processing in Examples 1, 2, 4, 8, 10, 17, and 24 of the present invention.

Embodiments for Carrying Out the Invention

[0029] Hereunder, embodiments of the present invention will be explained in detail; but the present invention is not limited to only the following embodiments.

[0030] In the present invention, the nickel microparticle is a microparticle made mainly of nickel metal. A nickel microparticle hydroxylated or oxidized at least in part is also called a nickel microparticle. In addition, the nickel microparticle can also be one containing an element(s) other than nickel to an extent not to affect the present invention. The nickel microparticle is not particularly restricted in particle diameter or crystallite diameter. As the nickel microparticles, ones that are commonly commercially available may be purchased and the modification method of the present invention may be applied thereto, or the modification method of the present invention may be applied to nickel microparticles separately prepared according to purpose.

[0031] In addition, nickel microparticles to which the modification method of the present invention is applicable can be any as long as weight loss thereof occurs due to heat treatment, and nickel microparticles produced by any method can be used such as ones prepared with a gas phase method and ones prepared with a liquid phase method, but the effect is particularly great when the nickel microparticles were prepared with a liquid phase method.

[0032] In the present invention, by making an acid and/or hydrogen peroxide act on the nickel microparticles mentioned

above, the effect of reducing the weight loss rate in simultaneous TG-DTA measurement can be obtained.

[0033] Applicant of the presently applied invention presumes, as to be described in detail hereinafter, that one of the reasons that nickel microparticles show weight loss is because nickel hydroxide is contained in part of the nickel microparticles.

[0034] FIG. 7 shows the results of a simultaneous TG-DTA measurement under a nitrogen atmosphere of nickel hydroxide. The measurement range is 40°C to 400°C. The TG curve shows a weight loss rate of about 19%, which is the ratio (a theoretical value) of water contained in nickel hydroxide ($\text{Ni}(\text{OH})_2$) from near 250°C, and in the entire measurement range, a weight loss rate of about 20%.

[0035] FIG. 4 shows the results of a simultaneous TG-DTA measurement of conventional nickel microparticles, which are described in Comparative Example 1 of the presently applied invention to be described later. The measurement range is 40°C to 400°C. Also in these results, the TG curve shows weight loss observed from near 250°C, and eventually shows a weight loss rate of about 1.25% in the entire measurement range, which approximates to the shape of the TG curve of nickel hydroxide mentioned above. That is, the weight loss at near 250°C or above indicates the possibility that a reaction including dehydration from nickel hydroxide was being effected, which is considered to lead to cracking and other defects in the burning process when a laminated ceramic condenser is produced.

[0036] Given this, it is considered that the problem of cracking and the like that occurs when, for example, producing a laminated ceramic condenser for an electrode of which nickel microparticles are used can be solved by reducing the weight loss in simultaneous TG-DTA measurement. It is deduced that nickel microparticles a certain amount or more of weight loss of which occurs will further form nickel hydroxide during storage under an air atmosphere.

[0037] The cause is not known exactly, but the inventor of the presently applied invention has confirmed that nickel microparticles with which the weight loss rate in simultaneous TG-DTA measurement mentioned above was over 1.0% formed nickel hydroxide in only a few days and were further increased in the weight loss rate in a simultaneous TG-DTA measurement.

[0038] As a result of performing modifying processing of nickel microparticles for reducing the weight loss rate in a simultaneous TG-DTA measurement of nickel microparticles, particularly, the weight loss rate in 40°C to 400°C to 1.0% or less, as to be described in detail hereinafter, the inventor of the presently applied invention has found that nickel microparticles can be produced which, even when stored for a long period of time, do not produce cracking and other defects in the burning process during production of a laminated ceramic condenser.

[0039] An illustrative example of the acid to be made to act on the abovementioned nickel microparticles includes inorganic acids such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, aqua regia, and mixed acid; and organic acids such as acetic acid and citric acid. A mixture of two or more kinds of acid may also be used. Although the mechanism by which the weight loss in simultaneous TG-DTA measurement of the nickel microparticles can be reduced by making any of the abovementioned acids act is not clear, it is considered that the reduction is due to dissolution of nickel hydroxide, etc. present on the surfaces of the particles or due to oxidation of nickel. Although the reason is not clear, the finding that by making an acid act on nickel microparticles, nickel hydroxide is not formed again and especially that further formation of nickel hydroxide does not occur with nickel microparticles with which the weight loss rate in simultaneous TG-DTA measurement mentioned above is 1.0% or less, was surprising even to the inventor of the presently applied invention. Therefore, even among the abovementioned acids, an acid capable of dissolving nickel hydroxide or an acid capable of oxidizing nickel is preferable, and especially among these, an oxidizing acid or a mixture of acids that includes an oxidizing acid is preferable, and it is further preferable to use nitric acid or a mixture of acids that includes nitric acid. In this case, it is preferable to add the nickel microparticles to the solvent containing the acid and to perform a stirring processing of a fixed time by ultrasonic processing or by use of any of various stirrers or to perform a microwave processing. The abovementioned acids also have the ability to dissolve the nickel microparticles and therefore a molar ratio of any of the abovementioned acids with respect to the nickel microparticles is preferably within a range of 0.001 to 0.1 and even more preferably within a range of 0.005 to 0.05. If the molar ratio falls below 0.001, the possibility that the effects of the present invention will not be obtained becomes high, and if the molar ratio exceeds 0.1, a problem such as dissolution of the nickel microparticles may occur.

[0040] As the hydrogen peroxide to be made to act on the abovementioned nickel microparticles, a commonly commercially available hydrogen peroxide water may be used. Although the mechanism by which the weight loss in simultaneous TG-DTA measurement of the nickel microparticles can be reduced by making the abovementioned hydrogen peroxide act is not clear, as in the case of making the acid act on the nickel microparticles, it is considered that the reduction is due to dissolution of nickel hydroxide, etc. present on the surfaces of the particles or due to oxidation of nickel or further due to oxidation of nickel hydroxide. A molar ratio of the abovementioned hydrogen peroxide with respect to the nickel microparticles is preferably within a range of 0.001 to 2.0 and even more preferably within a range of 0.001 to 1.0. Although in comparison to the abovementioned acid, the hydrogen peroxide is low in the possibility of dissolving the nickel microparticles, in view of the effect of reducing the weight loss, the molar ratio of the hydrogen peroxide with respect to the abovementioned nickel microparticles is preferably 1.0 or less. The present invention may also be carried out by replacing the hydrogen peroxide with ozone.

[0041] The processing of making any of the abovementioned acids act (acid processing) and the processing of making the hydrogen peroxide act (hydrogen peroxide processing) may be respectively carried out solely or both may be carried out. As illustrated in an embodiment to be described later, the weight loss rate in the simultaneous TG-DTA measurement can be reduced greatly by performing the hydrogen peroxide processing on the nickel microparticles on which the acid processing has been performed. Also, the same effect is provided by performing the acid processing on the nickel microparticles on which the hydrogen peroxide processing has been performed.

[0042] Preferably, the above-described acid processing and/or hydrogen peroxide processing are or is performed in any of various solvents. As examples of such solvents, water (tap water, RO water, pure water, etc.) and organic solvents (alcohol solvents, ketone solvents, ether solvents, aromatic solvents, carbon disulfide, aliphatic solvents, nitrile solvents, sulfoxide solvents, halogen solvents, ester solvents, and ionic solutions) can be cited. The present invention may be carried out by selecting one kind or a mixed solvent mixing two or more kinds from among such solvents according to purpose. In the present invention, in performing the above-described acid processing and/or hydrogen peroxide processing, it is preferable to use a ketone solvent such as acetone, methyl ethyl ketone, and cyclohexanone, and especially preferable to use acetone as the at least one kind of solvent.

[0043] An example of an embodiment of the present invention is to perform the above-described acid processing or hydrogen peroxide processing by preparing a solution by mixing any of the abovementioned acids or hydrogen peroxide to any of the abovementioned solvents, adding the nickel microparticles into the solution, and performing the stirring processing by ultrasonic processing or by use of any of various stirrers or performing the microwave processing.

[0044] In the stirring processing in the modification method according to the present invention, a known stirrer or stirring means may be used and stirring energy may be controlled as appropriate. Details concerning the stirring energy are described in Japanese Patent Laid-Open Publication No. H04-114725 by Applicant of the presently applied invention.

[0045] The method for stirring in the present invention is not particularly restricted and may be carried out using a stirrer or dissolver, emulsifier, disperser, homogenizer, etc. of any of various shearing types, a friction type, a high-pressure jet type, an ultrasonic type, etc. For example, a continuous type emulsifier, such as Ultra-Turrax (manufactured by IKA Japan K.K.), Polytron (manufactured by Kinematica AG), TK Homomixer (manufactured by PRIMIX Corporation), Ebara Milder (manufactured by EBARA CORPORATION), TK Homomic Line Flow (manufactured by PRIMIX Corporation), Colloid Mill (manufactured by Shinko Pantec Co., Ltd.), Slasher (manufactured by NIPPON COKE & ENGINEERING CO., LTD.), Trigonal Wet Pulverizer (manufactured by Mitsui Miike Chemical Engineering Machinery Co., Ltd.), Cavitron (manufactured by Eurotec, Ltd.), Fine Flow Mill (manufactured by Pacific Machinery & Engineering Co., Ltd.), a batch-type emulsifier, such as Clearmix (manufactured by M. Technique Co., Ltd.), Clearmix Dissolver (manufactured by M. Technique Co., Ltd.), FILMIX (manufactured by PRIMIX Corporation), or a combination continuous/batch-type emulsifier can be cited. Also, the stirring processing is preferably performed using a stirrer provided with a rotating stirring blade, especially the Clearmix (manufactured by M. Technique Co., Ltd.) or Clearmix Dissolver (manufactured by M. Technique Co., Ltd.) mentioned above.

[0046] An embodiment of applying the present invention to nickel microparticles produced using a microreactor shall now be described as an example.

Separation of nickel microparticle:

[0047] Firstly, a nickel-containing fluid, with which nickel metal or a nickel compound is dissolved or dispersed in a solvent, and a reducing agent fluid, containing a reducing agent, are prepared. The nickel compound is not particularly restricted, and an illustrative example thereof includes inorganic salts of nickel such as a nitrate, sulfate, chloride, and hydroxide of nickel and hydrates of such inorganic salts; and organic salts such as an acetate and acetylacetonate of nickel and organic solvates of such organic salts. These may be used solely or a plurality may be used. The reducing agent is not particularly restricted as long as it exhibits a property of reducing nickel ions, and an illustrative example thereof includes hydrides such as sodium borohydride; hydrazines; and polyvalent alcohols such as ethylene glycol. These may also be used solely or a plurality may be used by mixing or other method.

[0048] The abovementioned nickel-containing fluid and reducing agent fluid may be used upon mixing, dissolving, or dispersing the abovementioned nickel metal, nickel compound, or reducing agent in any of various solvents. As the abovementioned various solvents, the same solvents as the solvents used in the above-described acid processing and/or hydrogen peroxide processing may be used and a pH adjuster for adjusting the pH of the nickel-containing fluid and the reducing agent fluid may be added. An illustrative example of the pH adjuster includes inorganic or organic acidic substances such as hydrochloric acid, sulfuric acid, nitric acid, aqua regia, trichloroacetic acid, trifluoroacetic acid, phosphoric acid, citric acid, and ascorbic acid; alkali hydroxides such as sodium hydroxide and potassium hydroxide; basic substances such as amines including triethylamine and dimethylamino ethanol; and salts of these acidic substances and basic substances. These pH adjusters may be used solely or as a combination of two or more of them. Any of various stirrers may be used to prepare the abovementioned nickel-containing fluid and reducing agent fluid. The abovementioned fluids that have been prepared are mixed and the nickel component and the reducing agent component in

the fluids are made to react to separate the nickel microparticles. A case where a microreactor is used to mix the abovementioned fluids and separate the nickel microparticles shall be illustrated below.

[0049] In addition, as the microreactor, the one shown in FIG. 1, which is the same as the apparatuses described in Patent Document 6 and Patent Document 7, can be used. Hereunder, the microreactor will be described in detail. In

[0050] The microreactor (hereinafter, referred to also as an apparatus) of the present embodiment is provided with two processing members of a first processing member 10 and a second processing member 20 arranged opposite to each other, wherein the first processing member 10 rotates. The surfaces arranged opposite to each other of the respective processing members 10 and 20 are made to be the respective processing surfaces. The first processing member 10 is provided with a first processing surface 1 and the second processing member 20 is provided with a second processing surface 2.

[0051] Each of the processing surfaces 1 and 2 is connected to a flow path d1, d2 of the fluid to be processed and constitutes part of the flow path of the fluid to be processed. Distance between these processing surfaces 1 and 2 is controlled so as to form a minute space usually in the range of 1 mm or less, for example, 0.1 μm to 50 μm . With this, the fluid to be processed passing through between the processing surfaces 1 and 2 becomes a forced thin film fluid forced by the processing surfaces 1 and 2.

[0052] Moreover, this apparatus performs a fluid processing in which first and second fluids to be processed are reacted to separate nickel microparticles between the processing surfaces 1 and 2.

[0053] To more specifically explain, this apparatus is provided with a first holder 11 for holding the first processing member 10, a second holder 21 for holding the second processing member 20, a surface-approaching pressure imparting mechanism 43, a rotation drive mechanism (not shown in drawings), a first introduction part d1, a second introduction part d2, and fluid pressure imparting mechanisms p1 and p2. The fluid pressure imparting mechanisms p1 and p2 can be compressors or other pumps.

[0054] In the abovementioned embodiment, the first processing member 10 and the second processing member 20 are disks with ring forms. Material of the processing members 10 and 20 is not only metal but also carbon, ceramics, sintered metal, abrasion-resistant steel, sapphire, and other metal subjected to hardening treatment, and rigid material subjected to lining, coating, or plating. In the processing members 10 and 20 of abovementioned embodiment, the first and the second surfaces 1 and 2 arranged opposite to each other are mirror-polished, and arithmetic average roughness is 0.01 μm to 1.0 μm .

[0055] In the abovementioned embodiment, the second holder 21 is fixed to the apparatus, the first holder 11 attached to a rotary shaft 50 of the rotation drive mechanism fixed to the same apparatus rotates, and thereby the first processing member 10 attached to this first holder 11 rotates relative to the second processing member 20. As a matter of course, the second processing member 20 may be made to rotate, or the both may be made to rotate.

[0056] In the present invention, the rotation can be set to a speed of, for example, 350 to 5000 rpm.

[0057] In the abovementioned embodiment, the second processing member 20 approaches and separates from the first processing member 10 in the direction of the rotary shaft 50, wherein a side of the second processing member 20 opposite to the second processing surface 2 is accepted in an accepting part 41 arranged in the second holder 21 so as to be able to rise and set. However, in contrast to the above, the first processing member 10 may approach and separate from the second processing member 20, or both the processing members 10 and 20 may approach and separate from each other.

[0058] The abovementioned accepting part 41 is a concave portion for accepting the side of the second processing member 20 opposite to the second processing surface 2, and this concave portion is a groove being formed into a ring. This accepting part 41 accepts the second processing member 20 with sufficient clearance so that the side of the second processing member 20 opposite to the second processing surface 2 may rise and set.

[0059] The surface-approaching pressure imparting mechanism is a mechanism to generate force (hereinafter, surface-approaching pressure) to press the first processing surface 1 of the first processing member 10 and the second processing surface 2 of the second processing member 20 in the direction to make them approach each other. The mechanism generates a thin film fluid having minute thickness in a level of nanometer or micrometer while keeping the distance between the processing surfaces 1 and 2 in a predetermined minute distance by the balance between the surface-approaching pressure and the force due to the fluid pressure to separate the processing surfaces 1 and 2 from each other. In the abovementioned embodiment, the surface-approaching pressure imparting mechanism supplies the surface-approaching pressure by biasing the second processing member 20 toward the first processing member 10 by a spring 43 arranged in the second holder 21.

[0060] In addition, the first fluid to be processed which is pressurized with the fluid pressure imparting mechanism p1 is introduced from the first introduction part d1 to the space inside the processing members 10 and 20.

[0061] On the other hand, the second fluid to be processed which is pressurized with the fluid pressure imparting mechanism p2 is introduced from the second introduction part d2 via a path arranged inside the second processing member 20 to the space inside the processing members 10 and 20 through an opening d20 formed in the second

processing surface.

[0062] At the opening d20, the first fluid to be processed and the second fluid to be processed converge and mix with each other.

[0063] At this time, the mixed fluid to be processed becomes a forced thin film fluid by the processing surfaces 1 and 2 that keep the minute space therebetween, whereby the fluid is forced to move out from the circular, processing surfaces 1 and 2. The first processing member 10 is rotating; and thus, the mixed fluid to be processed does not move linearly from inside the circular, processing surfaces 1 and 2 to outside thereof, but does move spirally from the inside to the outside thereof by a resultant vector acting on the fluid to be processed, the vector being composed of a moving vector toward the radius direction of the circle and a moving vector toward the circumferential direction.

[0064] Here, as shown in FIG. 2, in the first processing surface 1 of the first processing member 10, a groove-like depression 13 extended toward an outer side from the central part of the first processing member 10, namely in a radius direction, may be formed. The depression 13 may be, as a plane view, curved or spirally extended on the first processing surface 1, or, though not shown in the drawing, may be extended straight radially, or bent at a right angle, or jogged; and the concave portion may be continuous, intermittent, or branched. In addition, this depression 13 may be formed also on the second processing surface 2, or on both the first and second processing surfaces 1 and 2. By forming the depression 13 as mentioned above, the micro-pump effect can be obtained so that the fluid to be processed may be sucked into between the first and second processing surfaces 1 and 2.

[0065] It is preferable that the base edge of the depression 13 reach the inner periphery of the first processing member 10. The front edge of the depression 13 is extended to the direction of the outer periphery of the first processing surface 1; the depth thereof is made gradually shallower (smaller) from the base edge to the front edge. Between the front edge of the depression 13 and the outer peripheral of the first processing surface 1 is formed a flat plane 16 not having the depression 13.

[0066] The opening d20 described above is arranged preferably at a position opposite to the flat surface of the first processing surface 1. The opening d20 is arranged especially preferably at a position opposite to the flat surface 16 located in the downstream of a position where the direction of flow of the first fluid to be processed upon introduction by the micro-pump effect is changed to the direction of a spiral and laminar flow formed between the processing surfaces. With this, mixing of a plurality of fluids to be processed and separation of the microparticles therefrom can be effected under the condition of a laminar flow.

[0067] The second introduction part d2 preferably has directionality. For example, the direction of introduction from the opening d20 of the second processing surface 2 may be inclined at a predetermined elevation angle relative to the second processing surface 2, and introduction from the opening d20 of the second processing surface 2 may have directionality in a plane along the second processing surface 2, and the direction of introduction of this second fluid may be in the outward direction departing from the center in a radial component of the processing surface and in the forward direction in a rotation component of the fluid between the rotating processing surfaces. As mentioned above, the flow of the first fluid to be processed at the opening d20 is a laminar flow and the second introduction part d2 has directionality, whereby the second fluid to be processed can be introduced between the processing surfaces 1 and 2 while suppressing the generation of turbulence to the flow of the first fluid to be processed.

[0068] In addition, the fluid discharged to outside the processing members 10 and 20 is collected via a vessel v into a beaker b as a discharged solution. In the embodiment of the present invention, the discharged solution contains nickel microparticles as to be described later.

[0069] Although, in the embodiment shown in FIG. 1, kinds of the fluid to be processed and numbers of the flow path thereof are set two respectively, they may be three or more. The opening for introduction arranged in each processing member is not particularly restricted in its form, size, and number; and these may be changed as appropriate. For example, as shown in FIG. 1, shape of the opening d20 may be a concentric circular ring shape which encircles the central opening of the processing surface 2 having a form of a ring-like disk, and the opening having the circular ring shape may be any of continuous and discontinuous. The opening for introduction may be arranged just before the first and second processing surfaces 1 and 2 or in the side of further upstream thereof.

[0070] In the present invention, it is good enough only if the processing could be effected between the processing surfaces 1 and 2, and a method wherein the second fluid to be processed is introduced from the first introduction part d1 and a solution containing the first fluid to be processed is introduced from the second introduction part d2 may also be used. For example, the expression "first" or "second" for each fluid has a meaning for merely discriminating an n^{th} fluid among a plurality of the fluids present; and therefore, a third or more fluids can also exist as in the foregoing.

[0071] By applying acid processing and/or hydrogen peroxide processing of the present invention to the nickel microparticles obtained using the microreactor mentioned above, the uniform and homogeneous nickel microparticles can be provided with an effect of reducing the weight loss in simultaneous TG-DTA measurement, particularly, an effect of reducing the weight loss that is observed from near 250°C, and long-term storage stability such as suppressing the formation of nickel hydroxide.

[0072] As described above, the nickel microparticles are microparticles made mainly of nickel metal in the present

invention. The nickel microparticles can be from any source. The modification method of the present invention may be applied to commonly commercially available nickel microparticles, or the modification method of the present invention may be applied to nickel microparticles separately prepared according to purpose.

[0073] In addition, nickel microparticles to which the modification method of the present invention is applicable can be any as long as weight loss thereof occurs due to heat treatment, and can be produced by any method. The modification method of the present invention is applicable to all nickel microparticles weight loss of which occurs due to heat treatment among nickel microparticles that exist in the world, and the modifying effect is particularly great on nickel microparticles prepared with a liquid phase method.

[0074] Further, nickel microparticles modified by the modification method of the present invention do not require heat treatment.

[0075] Regarding these nickel microparticles, particularly, ones produced by separating nickel microparticles using a liquid phase method, the nickel microparticles are preferably washed using a solvent such as pure water and then dried, and it is preferable to apply the modification method of the present invention to washed and dried nickel microparticle powders, that is, to perform acid processing and/or hydrogen peroxide processing on washed and dried nickel microparticle powders.

[0076] On the surface of unwashed nickel microparticles, various substances used for the separation reaction such as, for example, a reducing agent and its decomposed matter remain, and if acid processing and/or hydrogen peroxide processing is performed using the unwashed nickel microparticles, the substances may provide an adverse effect such that the amount of an acid and/or hydrogen peroxide to be used for the acid processing and/or hydrogen peroxide processing is increased.

Examples

[0077] Hereinafter, Examples and the like that specifically describe the constitution and effect of the present invention will be exemplified; but the present invention is not limited only to these Examples.

[0078] Firstly, description will be given of a method of preparing a nickel-containing fluid as solution A and a reducing agent fluid as solution B, mixing the solution A and the solution B using a microreactor to separate nickel microparticles, and applying the modification method of the present invention to the obtained nickel microparticles for producing nickel microparticles.

[0079] ULREA SS-11 (manufactured by M. Technique Co., Ltd.) was used as the microreactor. In this case, the solution A corresponds to a first fluid to be processed that is introduced from the first introduction part d1 of the microreactor shown in FIG. 1, and the solution B corresponds to a second fluid to be processed that is introduced from the second introduction part d2 of the same. The first introduction part d1 and the second introduction part d2 can be switched arbitrarily. Obtained nickel microparticles were analyzed under the following conditions.

[0080] XRD measurement was made by using the powder X-ray diffraction measurement instrument (product name: Empyrean, manufactured by PANalytical B. V.). The measurement conditions were as follows: measurement range of 10 to 100°, Cu anticathode, tube voltage of 45 kV, tube current of 40 mA, Bragg-Brentano HD (BBHD) used as an optical system, and scanning speed of 9°/min. The crystallite diameter D was calculated with use of the peak appeared near to 44° by using the Scherrer's equation with reference to the silicon polycrystal plate.

$$D = K \cdot \lambda / (\beta \cdot \cos \theta) \dots \text{Scherrer's equation:}$$

[0081] Here, K is the Scherrer's constant provided as K=0.9, and λ is the wavelength of the X-ray tube used, β is the half-width, and θ is the diffraction angle.

[0082] TEM observation was made by using the transmission electron microscope JEM-2100 (manufactured by JEOL Ltd.). The observation condition with the acceleration voltage of 200 kV was used.

[0083] SEM observation was made by using the scanning electron microscope JFM-7500F (manufactured by JEOL Ltd.). The observation conditions with the acceleration voltage of 5 kV and the magnification of 50,000 or more were used. The average particle diameter was the average value of the particle diameter measurements of 100 particles.

[0084] A simultaneous TG-DTA measurement was made using the simultaneous high-temperature differential scanning calorimetry/thermogravimetric analyzer TG/DTA6300 (manufactured by Hitachi, Ltd.) was used. The measurement conditions were as follows: alumina used as a reference, rate of temperature increase of 5°C/min., measurement range of 40 to 400°C and measurement under a nitrogen atmosphere. A weight loss rate from 40°C, which is at the start of measurement, to 400°C was confirmed. In addition, the weight of the sample was provided as 45 mg (± 2 mg).

Separation of nickel microparticle:

[0085] Solution A was prepared by mixing and dissolving each of the nickel sulfate hexahydrate/concentrated sulfuric acid/ethylene glycol/pure water (weight ratio of 2.33/0.86/83.54/13.27) by stirring for 60 minutes with a rotation number of 20000 rpm and a processing temperature of 24 to 60°C using a high-speed emulsification/dispersion apparatus Cleamix (product name: CLM-2.2S, manufactured by M. Technique Co., Ltd.). Solution B was prepared by mixing and dissolving each of the hydrazine monohydrate/sodium hydroxide/pure water (weight ratio of 70/5/25) by stirring for 30 minutes with a rotation number of 20000 rpm and a processing temperature of 25°C using the same high-speed emulsification/dispersion apparatus Cleamix (product name: CLM-2.2S, manufactured by M. Technique Co., Ltd.).

[0086] The solution A was introduced at 165°C and 600 ml/min. from the first introduction part d1 of the microreactor shown in FIG. 1 between the processing surfaces 1 and 2, and while the processing member 10 was rotated at 1700 rpm, the solution B was introduced at 60°C and 65 ml/min. from the second introduction part d2 between the processing surfaces 1 and 2, whereby the solution A and the solution B were mixed between the processing surfaces 1 and 2 to separate nickel microparticles. A slurry liquid containing the nickel microparticles separated between the processing surfaces 1 and 2 was discharged from between the processing surfaces 1 and 2, and collected via the vessel v into the beaker b.

Washing of Nickel Microparticle

[0087] The discharged solution collected into the beaker b was allowed to stand until it was cooled to 60°C or less, and the nickel microparticles were settled. The PH of the discharged solution was 8.45 (measurement temperature: 42.5°C). The supernatant solution in the beaker b was removed, and pure water 20 to 1500 times the weight of the settled nickel microparticles was added, and stirred for five minutes with a rotation number of 6000 rpm and a processing temperature of 25°C using Cleamix 2.2S to wash the nickel microparticles. The washing operation was repeated for 3 times, and then the nickel microparticles were again settled, and the supernatant solution was removed to obtain an aqueous wet cake (1) of nickel microparticles.

Drying of Nickel Microparticle

[0088] The aqueous wet cake (1) of nickel microparticles was dried at -0.10 MpaG and 20°C for 15 hours or more to obtain nickel microparticle powders. The content of water in the nickel microparticle powders was 89 µg/g. It is preferable to dry the nickel microparticle powders until the content of water therein becomes 1000 µg/g or less, preferably, 500 µg/g or less, and more preferably, 100 µg/g or less. A SEM picture of the nickel microparticle powders after drying is shown in FIG. 3 as Comparative Example 1 of the presently applied invention, and XRD measurement results thereof, in FIG. 10(A), and an enlarged view of the essential part of the XRD measurement results thereof, in FIG. 11 (spectrum (A)). From the SEM observation results, the average particle diameter of the nickel microparticles was 86.4 nm, and from the XRD measurement results, the crystallite diameter was 41.5 nm. In addition, a dispersion solution obtained by dispersing the nickel microparticle powders after drying in acetone was allowed to drip onto a collodion film to obtain a TEM observation sample. A TEM picture is shown in FIG. 8. As shown in FIG. 8, a thin membranous substance was observed on the surface of the nickel microparticles. Moreover, in the XRD measurement results (FIG. 11), peaks derived from nickel hydroxide were detected besides peaks derived from nickel, and it was confirmed that 3.4% by weight of nickel hydroxide was contained in the nickel powder. In FIG. 11, the peaks with filled circles are the peaks of nickel hydroxide. Further, results of a simultaneous TG-DTA measurement of the nickel microparticle powders after drying are shown in FIG. 4. Weight loss of 1.256% was confirmed in the measurement range mentioned above.

Temporal Change of Nickel Microparticle

[0089] A SEM picture of nickel microparticles after the nickel microparticle powders of Comparative Example 1 mentioned above were stored for two weeks under an air atmosphere is shown in FIG. 6, and XRD measurement results thereof, in FIG. 10(B), and an enlarged view of the essential part of the XRD measurement results thereof, in FIG. 11 (spectrum (B)). As can be understood by comparing with FIG. 3, in FIG. 6, a substance that seemed to have separated due to a temporal change was observed between the nickel microparticles.

[0090] In addition, it was understood in the XRD measurement results after storing for two weeks under an air atmosphere (FIG. 10(B), FIG. 11) that nickel hydroxide was increased to 16.2% by weight due to a temporal change during the storage. Moreover, in the measurement range, the weight loss rate in the simultaneous TG-DTA measurement showed an increase to 1.692%. It is deduced from the above that, as a result of storing for two weeks under an air atmosphere, part of the nickel microparticles have changed to nickel hydroxide and the weight loss rate has increased due to the change.

Example 1: Acid processing

[0091] 0.15 g of the nickel microparticle powders of Comparative Example 1 mentioned above was charged into 14.85 g of a solution obtained by mixing nitric acid/water/acetone at a weight ratio of 0.005/0.003/99.992 and subjected to a stirring processing for 15 minutes with a processing temperature of 20°C by a ultrasonic disperser (UP200S, manufactured by Hielscher Ultrasonics GmbH) to thereby perform acid processing on the nickel microparticles. After the acid processing, the nickel microparticles in the solution were settled, the supernatant solution was removed, and pure water 20 to 1500 times the weight of the nickel microparticles was added and washed the nickel microparticles by the ultrasonic cleaner described above. The washing operation was repeated for 3 times, and an aqueous wet cake (2) of nickel microparticles obtained after the washing was prepared, and then, the aqueous wet cake (2) was dried at -0.10 MpaG and 20°C for 15 hours or more to obtain nickel microparticle powders. The content of water in the nickel microparticle powders was 36 µg/g. It is preferable to dry the nickel microparticle powders until the content of water therein becomes 1000 µg/g or less, preferably, 500 µg/g or less, and more preferably, 100 µg/g or less.

Effect of Example 1

[0092] A dispersion solution obtained by dispersing the nickel microparticle powders obtained by the acid processing in acetone was allowed to drip onto a collodion film to obtain a TEM observation sample. A TEM picture is shown in FIG. 9. Unlike the TEM picture before the acid processing, that is, the TEM picture (FIG. 8) of the nickel microparticles obtained in Comparative Example 1, no thin membranous substance was observed on the surface of the nickel microparticles. The thin membranous substance on the surface of nickel microparticles is a hydroxide of nickel, and considered to be the thin membranous substance dissolved by the acid processing. Results of a simultaneous TG-DTA measurement of the nickel microparticle powders after the acid processing are shown in FIG. 5. The weight loss rate was 0.793%. By thus subjecting nickel microparticles to acid processing by an acetone solution containing nitric acid, the weight loss rate in the simultaneous TG-DTA measurement could be reduced as compared with Comparative Example 1. In addition, XRD measurement results of the nickel microparticle powders obtained in Example 1 are shown in FIG. 12(A). As shown in FIG. 12(A), no peaks derived from nickel hydroxide were detected.

[0093] As a result of a simultaneous TG-DTA measurement performed again after storing the nickel microparticle powders for two weeks under an air atmosphere, the weight loss rate in the measurement range mentioned above showed a further reduction to 0.643%. It was understood that the nickel microparticles (Comparative Example 1) without having been subjected to the acid processing of the present invention showed an increase in the weight loss rate in the simultaneous TG-DTA measurement due to storage for two weeks under an air atmosphere, whereas the nickel microparticles (Example 1) with having been subjected to the acid processing of the present invention, even when stored under an air atmosphere, provides an effect of reducing the weight loss rate from before the storage.

[0094] With the nickel microparticles applied with the acid processing of Example 1, even when this was stored for a month under an air atmosphere, no such substance that seemed to have separated as observed in the SEM picture of FIG. 6 described above was confirmed, and there was also no change in XRD measurement results from those immediately after the acid processing, and no peaks derived from nickel hydroxide were detected. It was understood by this that applying the acid processing of the present invention to nickel microparticles can reduce the weight loss rate in simultaneous TG-DTA measurement, and further can suppress the formation of nickel hydroxide during long-term storage.

Example 2: Processing of making acid act on nickel microparticles using stirrer provided with rotating stirring blade

[0095] 15 g of the nickel microparticle powders of Comparative Example 1 mentioned above was charged into 1485 g of a solution obtained by mixing nitric acid/water/acetone at a weight ratio of 0.005/0.003/99.992 and stirred for 15 minutes with a processing temperature of 20°C by a high-speed emulsification/dispersion apparatus Cleamix (product name: CLM-2.2S, manufactured by M. Technique Co., Ltd.) to thereby perform acid processing on the nickel microparticles. After the acid processing, the nickel microparticles in the solution were settled, the supernatant solution was removed, and pure water 20 to 700 times the weight of the nickel microparticles was added and washed the nickel microparticles using Cleamix. The washing operation was repeated for 3 times, and an aqueous wet cake (3) of nickel microparticles obtained after the washing was prepared, and then, the aqueous wet cake (3) was dried at -0.10 MpaG and 20°C for 15 hours or more to obtain nickel microparticle powders.

Effect of Example 2

[0096] From the results of a simultaneous TG-DTA measurement after the acid processing, the weight loss rate was 0.644%, and the weight loss rate in the simultaneous TG-DTA measurement could be reduced as compared with

Comparative Example 1. In addition, XRD measurement results of the nickel microparticle powders obtained in Example 2 are shown in FIG. 12 (C). As shown in FIG. 12(C), no peaks derived from nickel hydroxide were detected. As a result of a simultaneous TG-DTA measurement performed again after storing the nickel microparticles for two weeks under an air atmosphere, the weight loss rate in the measurement range mentioned above showed a reduction to 0.533%. This way, performing acid processing using a stirrer provided with a rotating stirring blade proves to be further effective for a reduction in weight loss.

[0097] In addition, other examples of acid processing; Example 3 to Example 7 and Example 16 to Example 19, which were changed in the method for separating nickel microparticles or in the molar ratio of an acid to nickel microparticles when acid processing was performed will be described later. The molar ratio of an acid to nickel microparticles when acid processing was performed was changed by adjusting the weight ratio of nitric acid/water/acetone in the solution (ultrasonic disperser: 14.85 g, stirrer: 1485 g) to be used for the acid processing relative to the nickel microparticle powders (ultrasonic disperser: 0.15 g, stirrer: 15 g) to be subjected to the acid processing.

Example 8: Hydrogen peroxide processing

[0098] Explanation will be made as to a processing (hydrogen peroxide processing) for which an acid was changed to hydrogen peroxide in the processing of making an acid act on nickel microparticles of Example 1. 0.15 g of the nickel microparticles of Comparative Example 1 mentioned above was charged into 14.85 g of a solution obtained by mixing hydrogen peroxide/water/acetone at a weight ratio of 0.005/0.012/99.983 and stirred for 15 minutes with a processing temperature of 20°C by a ultrasonic disperser (UP200S, manufactured by Hielscher Ultrasonics GmbH) to thereby perform a processing of making hydrogen peroxide act on the nickel microparticles. In the same manner as with the case of acid processing, after the hydrogen peroxide processing, the nickel microparticles in the solution were settled, the supernatant solution was removed, and pure water 20 to 1500 times the weight of the nickel microparticles was added and washed the nickel microparticles by the ultrasonic cleaner described above. The washing operation was repeated for 3 times, and an aqueous wet cake (4) of nickel microparticles obtained after the washing was prepared, and then, the aqueous wet cake (4) of nickel microparticles was dried at -0.10 MpaG and 20°C for 15 hours or more to obtain nickel microparticle powders. Similar to the case of acid processing, the content of water in the nickel microparticle powders was 42 µg/g. It is preferable to dry the nickel microparticle powders until the content of water therein becomes 1000 µg/g or less, preferably, 500 µg/g or less, and more preferably, 100 µg/g or less.

Effect of Example 8

[0099] As a result of TEM observation of the nickel microparticle powders obtained in Example 8 made by the same method as in Comparative Example 1, the thin membranous substance observed on the surface of the nickel microparticles obtained in Comparative Example 1 was not observed. From the results of a simultaneous TG-DTA measurement of the nickel microparticle powders after the hydrogen peroxide processing, the weight loss rate in the measurement range was 0.989%. By thus subjecting nickel microparticles to hydrogen peroxide processing by an acetone solution containing hydrogen peroxide, the weight loss rate in the simultaneous TG-DTA measurement could be reduced as compared with Comparative Example 1. In addition, XRD measurement results of the nickel microparticle powders obtained in Example 8 are shown in FIG. 12(B). As shown in FIG. 12(B), no peaks derived from nickel hydroxide were detected. As a result of a simultaneous TG-DTA measurement performed again after storing the nickel microparticle powders for two weeks under an air atmosphere, the weight loss rate in the measurement range mentioned above showed a further reduction to 0.741%. It was understood that the nickel microparticles (Comparative Example 1) without having been subjected to the hydrogen peroxide processing of the present invention showed an increase in the weight loss rate in the simultaneous TG-DTA measurement due to storage for two weeks under an air atmosphere, whereas the nickel microparticles (Example 8) with having been subjected to the hydrogen peroxide processing of the present invention, even when stored under an air atmosphere, provides an effect of reducing the weight loss rate from before the storage.

[0100] Similar to the nickel microparticles for which the acid processing of Example 1 was carried out, also with the nickel microparticles for which the hydrogen peroxide processing of Example 8 was carried out, even when this was stored for a month under an air atmosphere, no such substance that seemed to have separated as observed in the SEM picture of FIG. 6 mentioned above was confirmed, and there was also no change in XRD measurement results from those immediately after the hydrogen peroxide processing, and no peaks derived from nickel hydroxide were detected. It was understood by this that applying the hydrogen peroxide processing of the present invention to nickel microparticles can reduce the weight loss rate and amount in simultaneous TG-DTA measurement, and further can suppress the formation of nickel hydroxide during long-term storage. In addition, other examples changed in the method for separating nickel microparticles or in the molar ratio of hydrogen peroxide to nickel microparticles when hydrogen peroxide processing was performed; Example 9 to Example 14 and Example 20 to Example 23 will be described later. The molar ratio

of hydrogen peroxide to nickel microparticles when hydrogen peroxide processing was performed was changed by adjusting the weight ratio of hydrogen peroxide/water/acetone in the solution (ultrasonic disperser: 14.85 g, stirrer: 1485 g) to be used for the hydrogen peroxide processing relative to the nickel microparticle powders (ultrasonic disperser: 0.15 g, stirrer: 15 g) to be subjected to the hydrogen peroxide processing.

Example 15: Processing of making both of acid and hydrogen peroxide act on nickel microparticles

[0101] Explanation will be made as to Example 15 in which both of the acid processing and hydrogen peroxide processing mentioned above were applied to nickel microparticles.

[0102] 0.15 g of the nickel microparticle powders of Comparative Example 1 mentioned above was charged into 14.85 g of a solution obtained by mixing nitric acid/water/acetone at a weight ratio of 0.010/0.007/99.983 and stirred for 15 minutes with a processing temperature of 20°C by a ultrasonic disperser (UP200S, manufactured by Hielscher Ultrasonics GmbH) to thereby perform acid processing on the nickel microparticles.

[0103] After the acid processing, the nickel microparticles contained in the solution were settled, the supernatant solution was removed, and pure water 20 to 1500 times the weight of the nickel microparticles was added and the nickel microparticles were washed by the ultrasonic cleaner described above. The washing operation was repeated for 3 times, and an aqueous wet cake (5) of nickel microparticles obtained after the washing was prepared, and then, the aqueous wet cake (5) was dried at -0.10 MpaG and 20°C for 15 hours or more to obtain nickel microparticle powders.

[0104] 0.15 g of the obtained nickel microparticle powders was charged into 14.85 g of a solution obtained by mixing hydrogen peroxide/water/acetone at a weight ratio of 0.010/0.023/99.967 and stirred for 15 minutes with a processing temperature of 20 °C by the ultrasonic disperser described above to thereby perform hydrogen peroxide processing on the nickel microparticles.

[0105] After the hydrogen peroxide processing, the nickel microparticles contained in the solution were settled, the supernatant solution was removed, and pure water 20 to 1500 times the weight of the nickel microparticles was added and washed the nickel microparticles by the ultrasonic cleaner. The washing operation was repeated for 3 times, and an aqueous wet cake (6) of nickel microparticles obtained after the washing was prepared, and then, the aqueous wet cake (6) was dried at -0.10 MpaG and 20°C for 15 hours or more to obtain nickel microparticle powders.

Effect of Example 15

[0106] From the results of a simultaneous TG-DTA measurement after the hydrogen peroxide processing of the nickel microparticle powders, the weight loss in the measurement range mentioned above was 0.598%. By performing both of the acid processing and hydrogen peroxide processing mentioned above, the weight loss rate in the simultaneous TG-DTA measurement could be further reduced as compared with the case (Example 3, Example 10) where acid processing or hydrogen peroxide processing was carried out solely. In addition, from XRD measurement results of the nickel microparticle powders obtained in Example 15, no peaks derived from nickel hydroxide were detected. Moreover, also with the nickel microparticles for which both of the acid processing and hydrogen peroxide processing were carried out, even when this was stored for a month under an air atmosphere, no such substance that seemed to have separated as observed in the SEM picture of FIG. 6 mentioned above was confirmed, and also in XRD measurement results, no peaks derived from nickel hydroxide were detected. It is understood by this that applying both the acid processing and hydrogen peroxide processing to nickel microparticles can reduce the weight loss amount in simultaneous TG-DTA measurement, and further can suppress the formation of nickel hydroxide during long-term storage.

[0107] As a result of a simultaneous TG-DTA measurement performed again after storing the nickel microparticle powders for two weeks under an air atmosphere, the weight loss rate in the measurement range mentioned above showed a reduction to 0.492%. It was understood that the nickel microparticles of Comparative Example 1 showed an increase in the weight loss rate in the simultaneous TG-DTA measurement due to storage for two weeks under an air atmosphere, whereas the nickel microparticles with having been subjected to both of the acid processing and hydrogen peroxide processing of the present invention, by being stored under an air atmosphere, provides an effect of reducing the weight loss rate from before the storage. It was understood by this that applying both the acid processing and hydrogen peroxide processing of the present invention to nickel microparticles can reduce the weight loss rate and amount in simultaneous TG-DTA measurement, and further can suppress the formation of nickel hydroxide during long-term storage. In addition, Example 24 changed in the method for separating nickel microparticles will be described later.

Another Example Using Microreactor

[0108] Processing conditions and results of the acid processing or hydrogen peroxide processing mentioned above for nickel microparticles produced with the molar ratio of nitric acid or hydrogen peroxide to nickel microparticles changed when the acid processing or hydrogen peroxide processing was performed are shown in the following Table 1 together

with Examples 1, 2, 8, and 15. In addition, operation procedures that are not described are the same as the above. Moreover, the molar ratio of an acid to nickel microparticles when acid processing was performed was changed by adjusting the weight ratio of nitric acid/water/acetone in the solution (ultrasonic disperser: 14.85 g, stirrer: 1485 g) to be used for the acid processing relative to the nickel microparticle powders (ultrasonic disperser: 0.15 g, stirrer: 15 g) to be subjected to the acid processing, and the molar ratio of hydrogen peroxide to nickel microparticles when hydrogen peroxide processing was performed was changed by adjusting the weight ratio of hydrogen peroxide/water/acetone in the solution (ultrasonic disperser: 14.85 g, stirrer: 1485 g) to be used for the hydrogen peroxide processing relative to the nickel microparticle powders (ultrasonic disperser: 0.15 g, stirrer: 15 g) to be subjected to the hydrogen peroxide processing.

Table 1

		Apparatus used for processing	Processing temperature (°C)	Processing time (min.)	Molar ratio of acid or hydrogen peroxide to nickel microparticles	Weight loss rate (%) from measurement start to 400°C	Crystallite diameter (nm)
Comparative Example 1	Unprocessed	--	--	--	--	1.256	41.5
Example 1	(1) Acid processing	Ultrasonic disperser (UP200S)	20	15	0.005	0.793	41.3
Example 2		Stirrer (Cleamix)	20	15	0.005	0.644	42.8
Example 3		Ultrasonic disperser (UP200S)	20	15	0.009	0.791	42.4
Example 4		Ultrasonic disperser (UP200S)	20	15	0.012	0.762	43.1
Example 5		Ultrasonic disperser (UP200S)	20	15	0.019	0.785	41.9
Example 6		Ultrasonic disperser (UP200S)	20	15	0.037	0.813	41.5
Example 7		Ultrasonic disperser (UP200S)	20	15	0.093	0.794	41.3
Example 8		Ultrasonic disperser (UP200S)	20	15	0.009	0.989	41.1
Example 9		Ultrasonic disperser (UP200S)	20	15	0.014	0.782	41.0
Example 10		Ultrasonic disperser (UP200S)	20	15	0.017	0.644	42.8

		Apparatus used for processing	Processing temperature (°C)	Processing time (min.)	Molar ratio of acid or hydrogen peroxide to nickel microparticles	Weight loss rate (%) from measurement start to 400°C	Crystallite diameter (nm)
Example 11	(2) Hydrogen peroxide processing	Ultrasonic disperser (UP200S)	20	15	0.022	0.894	42.7
Example 12		Ultrasonic disperser (UP200S)	20	15	0.173	0.753	42.6
Example 13		Ultrasonic disperser (UP200S)	20	15	0.863	0.821	41.8
Example 14		Ultrasonic disperser (UP200S)	20	15	1.725	0.920	41.6
Example 15	(1)+(2)	Ultrasonic disperser (UP200S)	20	15	HNO ₃ : 0.009	0.598	43.2
					H ₂ O ₂ : 0.017		

[0109] It can be understood from Table 1 that the weight loss rate in simultaneous TG-DTA measurement reduces as a result of the acid processing and/or hydrogen peroxide processing being applied.

[0110] Also, XRD measurement results of the nickel microparticle powders obtained in Example 4 are shown in FIG. 12 (D), and XRD measurement results of the nickel microparticle powders obtained in Example 10 are shown in FIG. 12(E). In either example, no peaks derived from nickel hydroxide were detected in the XRD measurement results, and even after storage for a month under an air atmosphere, no such substance that seemed to have separated as observed in the SEM picture of FIG. 6 was confirmed, and no peaks derived from nickel hydroxide were detected in the XRD measurement results.

[0111] Further, according to Table 1, all examples resulted in crystallite diameters that have no problem with the application to a laminated ceramic condenser or the like.

Example by Batch Method

[0112] Next, as a batch method, the same solutions as those in Comparative Example 1 were used as solution A and solution B and the acid processing and/or hydrogen peroxide processing of the present invention was applied to nickel microparticles separated in a beaker. Processing conditions and results of the acid processing and/or hydrogen peroxide processing are shown in Table 2.

[0113] In the abovementioned batch method, with 600 ml of the solution A being stirred at 100°C in a beaker and at 150 rpm using a magnetic stirrer, 65 ml of the solution B was charged in a minute at 90°C, and then stirred for 60 minutes at 100°C and 150 rpm using a magnetic stirrer to separate nickel microparticles. Thereafter, in the same manner as with Comparative Example 1, washing and drying were performed, and the obtained nickel microparticle powders were used as Comparative Example 2, and for the nickel microparticles obtained in Comparative Example 2, acid processing and/or hydrogen peroxide processing was carried out using a ultrasonic disperser (UP200S, manufactured by Hielscher Ultrasonics GmbH) or a high-speed emulsification/dispersion apparatus Cleamix (product name: CLM-2.2S, manufactured by M. Technique Co., Ltd.). In addition, processing conditions that are not included in the table are the same as those of Examples 1 to 15. From SEM observation results, the average particle diameter of nickel microparticles of Comparative Example 2 was 116 nm, and from XRD measurement results, the crystallite diameter of Comparative Example 2 was 14.1 nm.

Table 2

		Processing temperature (°C)	Processing time (min.)	Molar ratio of acid or hydrogen peroxide to nickel microparticles	Weight loss rate (%) from measurement start to 400°C	Crystallite diameter (nm)
Comparative Example 2	Unprocessed	--	--	--	1.701	14.1
Example 16	(1) Acid processing	20	15	0.005	0.979	14.3
Example 17		20	15	0.009	0.859	15.1
Example 18		20	15	0.037	0.989	14.9
Example 19		20	15	0.093	0.899	14.9
Example 20	(2) Hydrogen peroxide processing	20	15	0.009	0.919	14.2
Example 21		20	15	0.017	0.949	15.2
Example 22		20	15	0.173	0.863	15.2
Example 23		20	15	1.725	0.894	14.6
Example 24	(1) + (2)	20	15	HNO ₃ : 0.009	0.687	15.6
				H ₂ O ₂ : 0.017		

[0114] It can be understood from Table 2 that, similar to the case of nickel microparticles (Comparative Example 1) produced using a microreactor, also with the nickel microparticles (Comparative Example 2) produced by a batch method, the weight loss rate in a simultaneous TG-DTA measurement reduces as a result of the acid processing and/or hydrogen peroxide processing being applied.

[0115] Also, XRD measurement results of the nickel microparticle powders obtained in Example 17 are shown in FIG. 12 (F), and XRD measurement results of the nickel microparticle powders obtained in Example 24 are shown in FIG. 12(G). In either example, no peaks derived from nickel hydroxide were detected in the XRD measurement results, and even after storage for a month under an air atmosphere, no such substance that seemed to have separated as observed in the SEM picture of FIG. 6 was confirmed, and no peaks derived from nickel hydroxide were detected in the XRD measurement results.

[0116] Further, according to Table 2, all examples resulted in crystallite diameters that have no problem with the application to a laminated ceramic condenser or the like.

[0117] It was understood from the above results that applying the acid processing and/or hydrogen peroxide processing of the present invention to nickel microparticles can reduce the weight loss rate in simultaneous TG-DTA measurement, and further can suppress the formation of nickel hydroxide during long-term storage.

Reference Signs List

[0118]

- 1 first processing surface
- 2 second processing surface
- 10 first processing member
- 11 first holder
- 20 second processing member
- 21 second holder
- d1 first introduction part
- d2 second introduction part
- d20 opening

Claims

1. A method for modifying nickel microparticles comprising a step of making an acid and/or hydrogen peroxide act on nickel microparticles weight loss of which occurs due to heat treatment such as burning.
2. The method for modifying nickel microparticles according to claim 1, wherein the step of making an acid and/or hydrogen peroxide act reduces a rate of weight loss due to heat treatment of the nickel microparticles.
3. The method for modifying nickel microparticles according to claim 2, wherein the rate of weight loss due to heat treatment of the nickel microparticles is a weight loss rate in simultaneous thermogravimetry-differential thermal analysis measurement, and the weight loss rate in a simultaneous thermogravimetry-differential thermal analysis measurement under a nitrogen atmosphere of the nickel microparticles is 1% or less in a range of 40°C to 400°C.
4. The method for modifying nickel microparticles according to any one of claims 1 to 3, wherein nitric acid or a mixture of acids that include nitric acid is used as the acid.
5. The method for modifying nickel microparticles according to any one of claims 1 to 4, wherein the nickel microparticles and acid and/or hydrogen peroxide are made to act in a ketonic solvent.
6. The method for modifying nickel microparticles according to any one of claims 1 to 5, wherein a molar ratio of the acid to the nickel microparticles is in a range of 0.001 to 0.1.
7. The method for modifying nickel microparticles according to any one of claims 1 to 6, wherein a molar ratio of the hydrogen peroxide to the nickel microparticles is in a range of 0.001 to 2.0.
8. The method for modifying nickel microparticles according to any one of claims 1 to 7, wherein the step of making

an acid and/or hydrogen peroxide act includes an ultrasonic processing, a stirring processing, or a microwave processing.

5 9. The method for modifying nickel microparticles according to claim 8, wherein the stirring processing is performed using a stirrer provided with a rotating stirring blade.

10. The method for modifying nickel microparticles according to any one of claims 1 to 9, wherein powder of the nickel microparticles on which the acid and/or hydrogen peroxide was made to act is stored under an air atmosphere.

10 11. The method for modifying nickel microparticles according to any one of claims 1 to 10, wherein the nickel microparticles are nickel microparticles separated by a microreactor which makes at least two kinds of fluids to be processed react.

15 12. A method for modifying nickel microparticles comprising a step of making a substance which reacts with nickel hydroxide act on nickel microparticles on at least surfaces of which nickel hydroxide is present to reduce the nickel hydroxide.

20 13. A method for producing nickel microparticles comprising the modification method according to any one of claims 1 to 12.

14. The method for producing nickel microparticles according to claim 13, being a method for producing the nickel microparticles using a microreactor, the said microreactor comprising:

25 a first processing surface and a second processing surface which are disposed facing each other so as to be able to approach and/or separate from each other, at least one of which rotates relative to the other, comprising:

a step of introducing at least two kinds of fluids to be processed between the first processing surface and the second processing surface;

30 a step of generating a separating force which acts in a direction to separate the first processing surface and the second processing surface from each other by an introducing pressure of the at least two kinds of fluids to be processed imparted to between the first processing surface and the second processing surface;

35 a step of forming a thin film fluid by making the at least two kinds of fluids to be processed converge with each other between the first processing surface and the second processing surface kept at a minute distance and pass through between the first processing surface and the second processing surface while keeping the minute distance between the first processing surface and the second processing surface by the separating force; and

40 a step of making the fluids to be processed react with each other in the thin film fluid and separating nickel microparticles by the reaction.

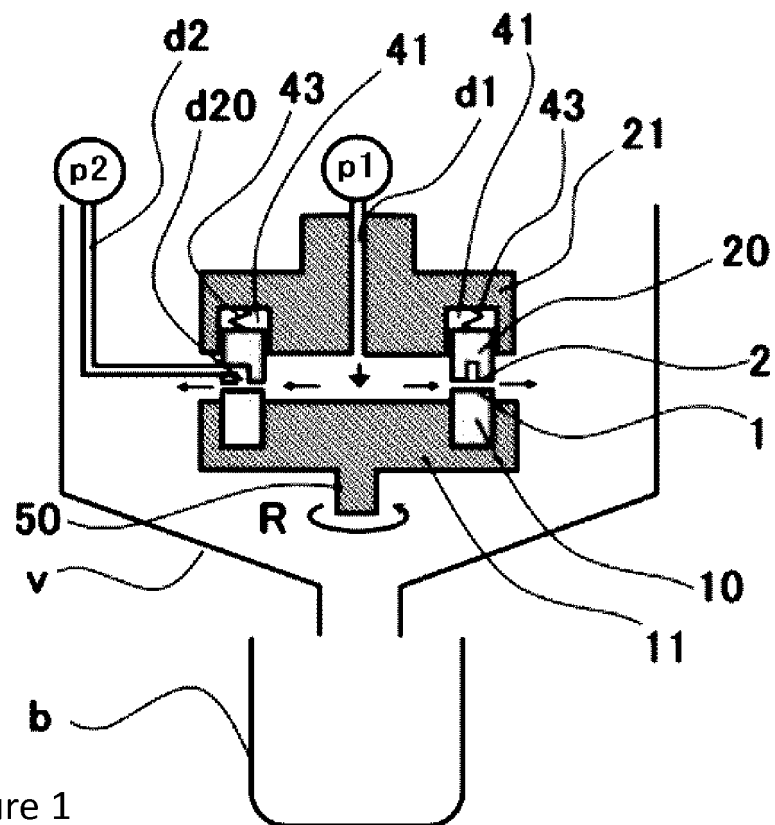


Figure 1

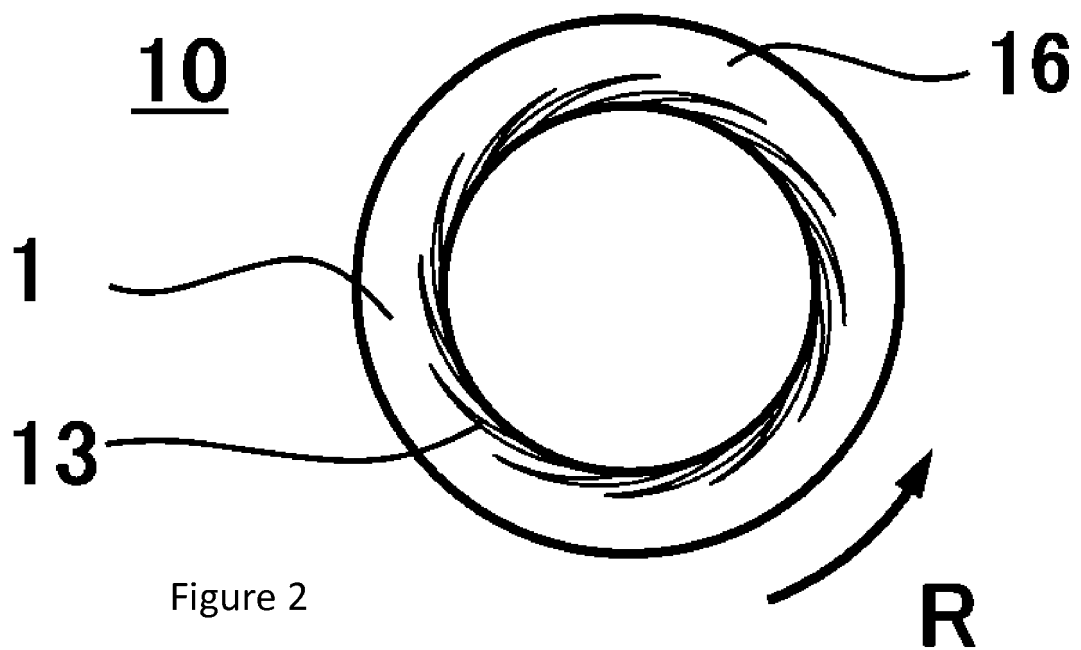


Figure 2

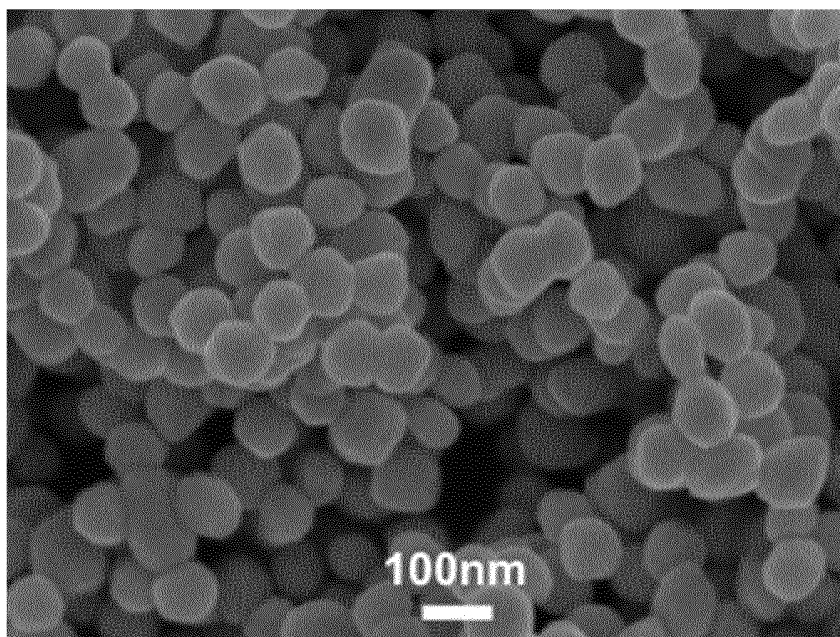


Figure 3

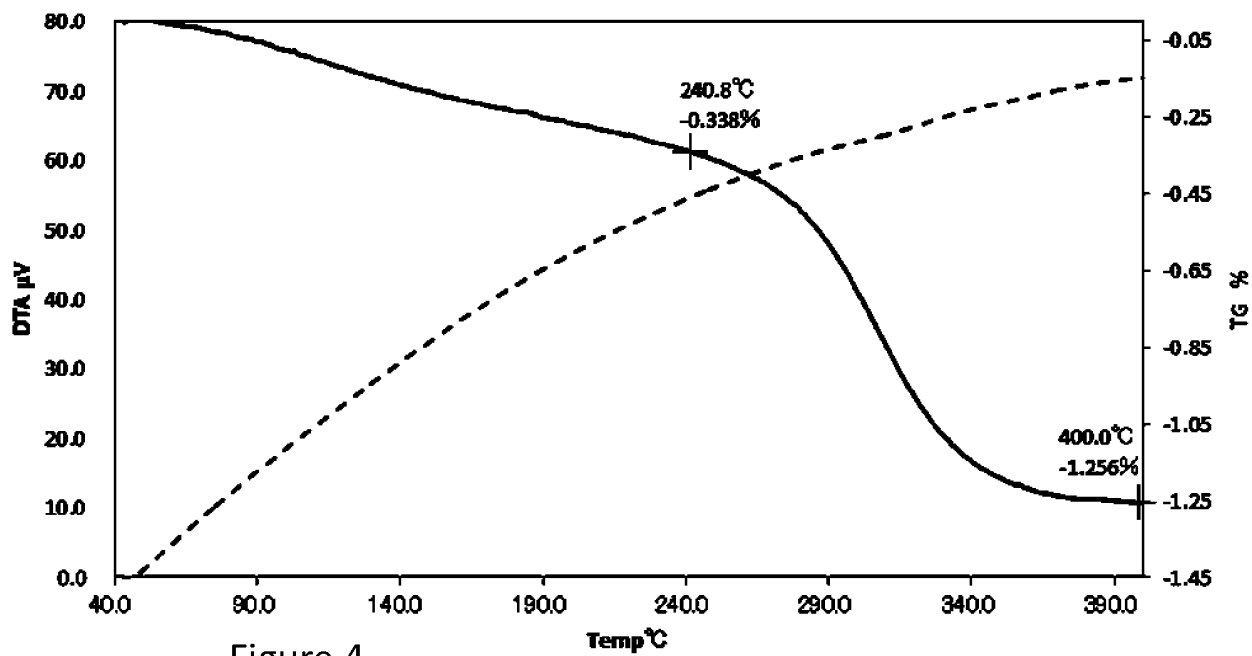


Figure 4

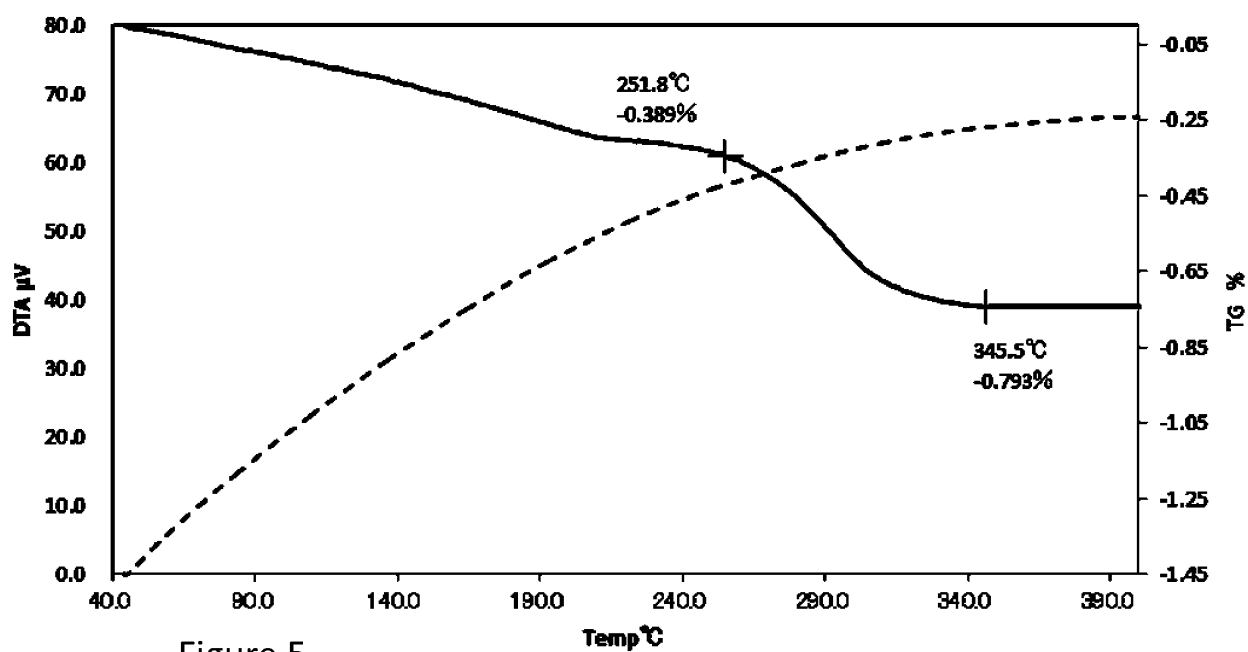


Figure 5

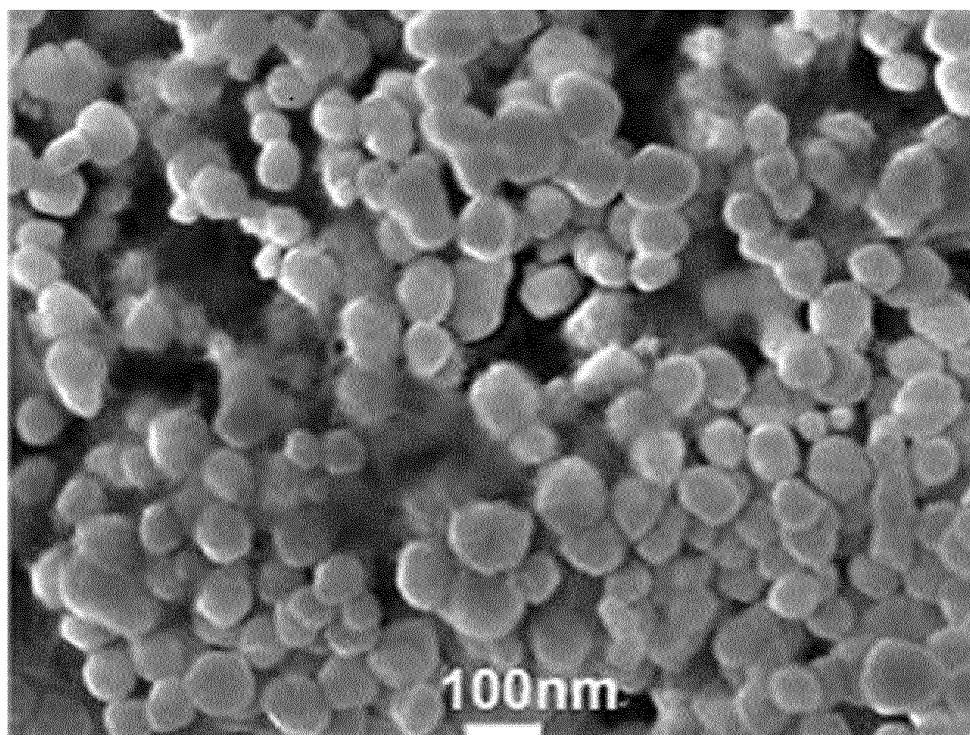


Figure 6

Figure 7

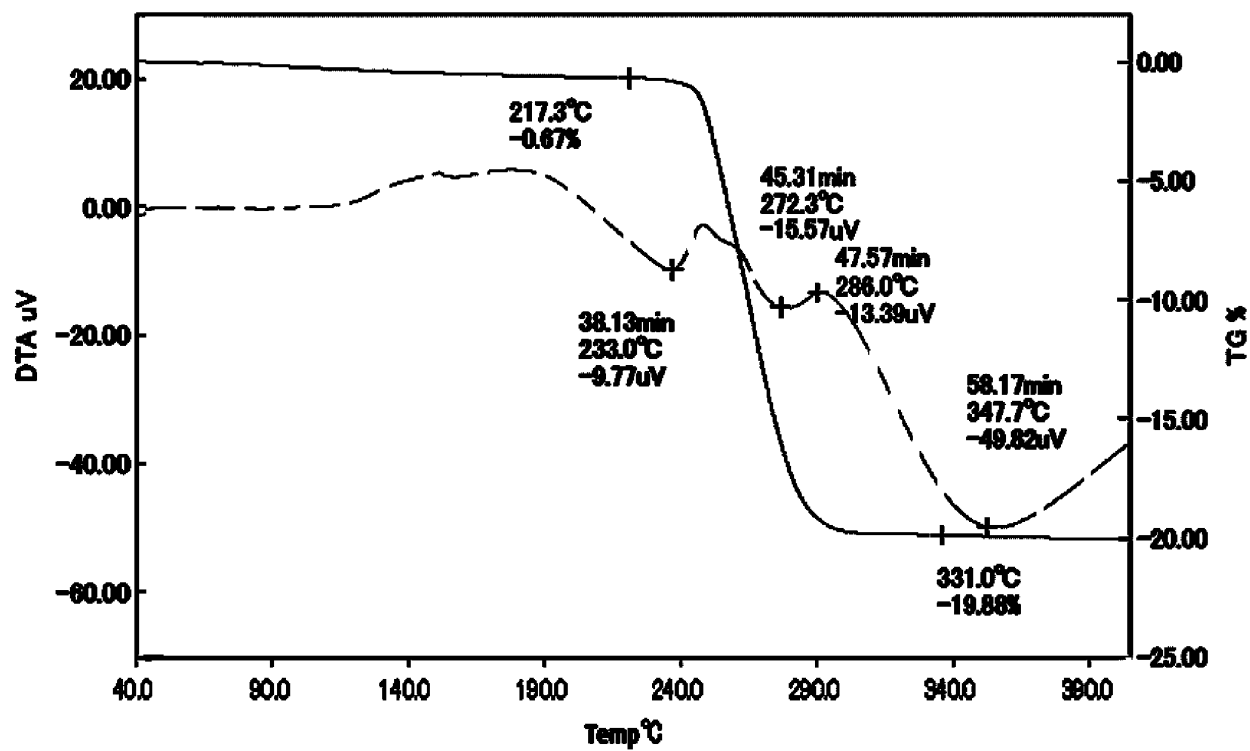


Figure 8

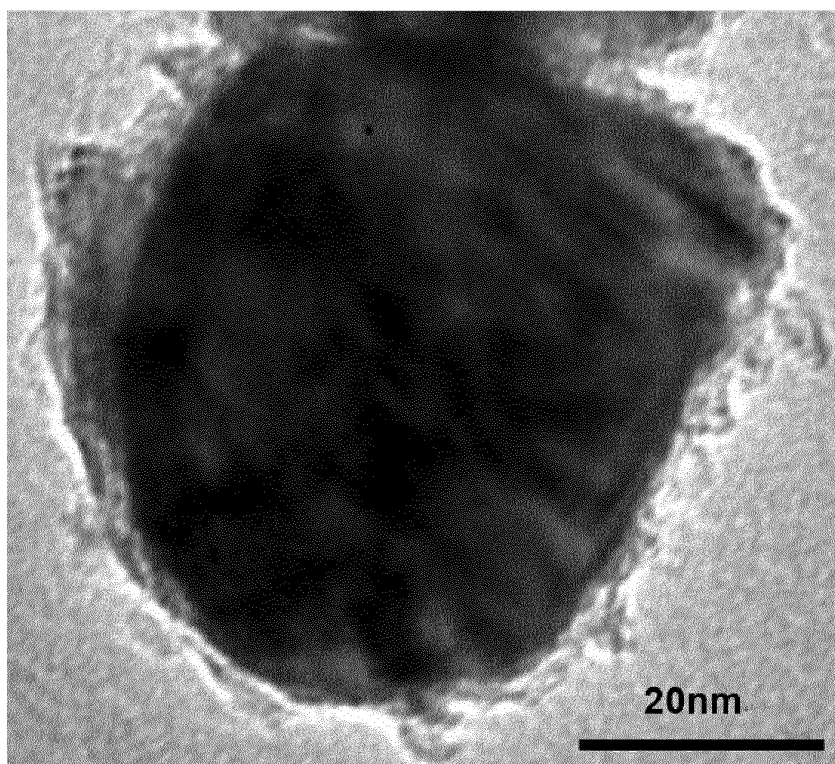


Figure 9

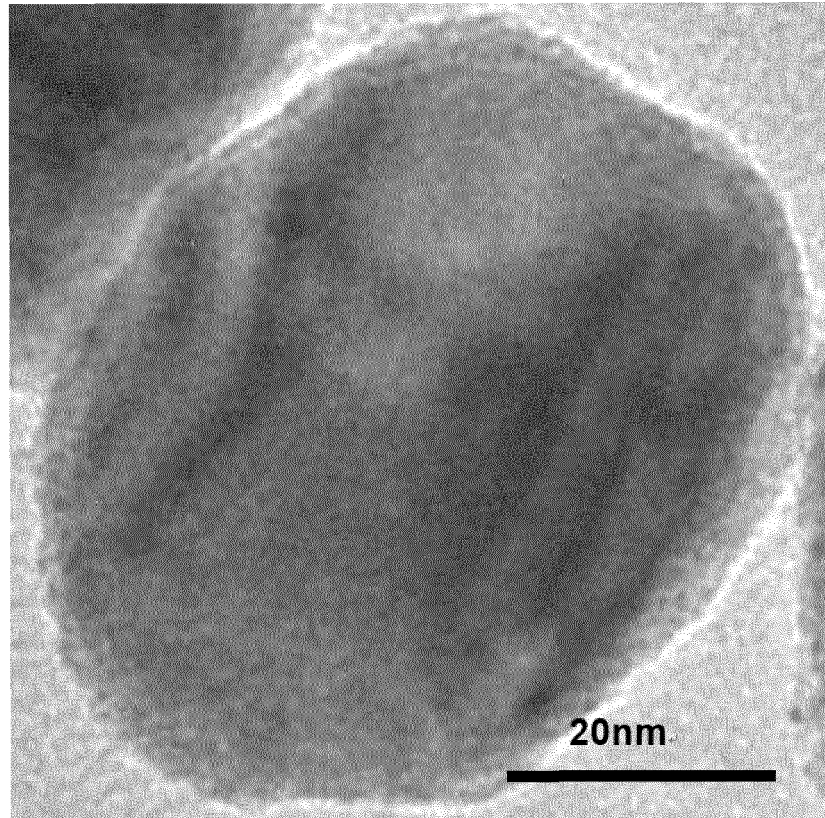


Figure 10

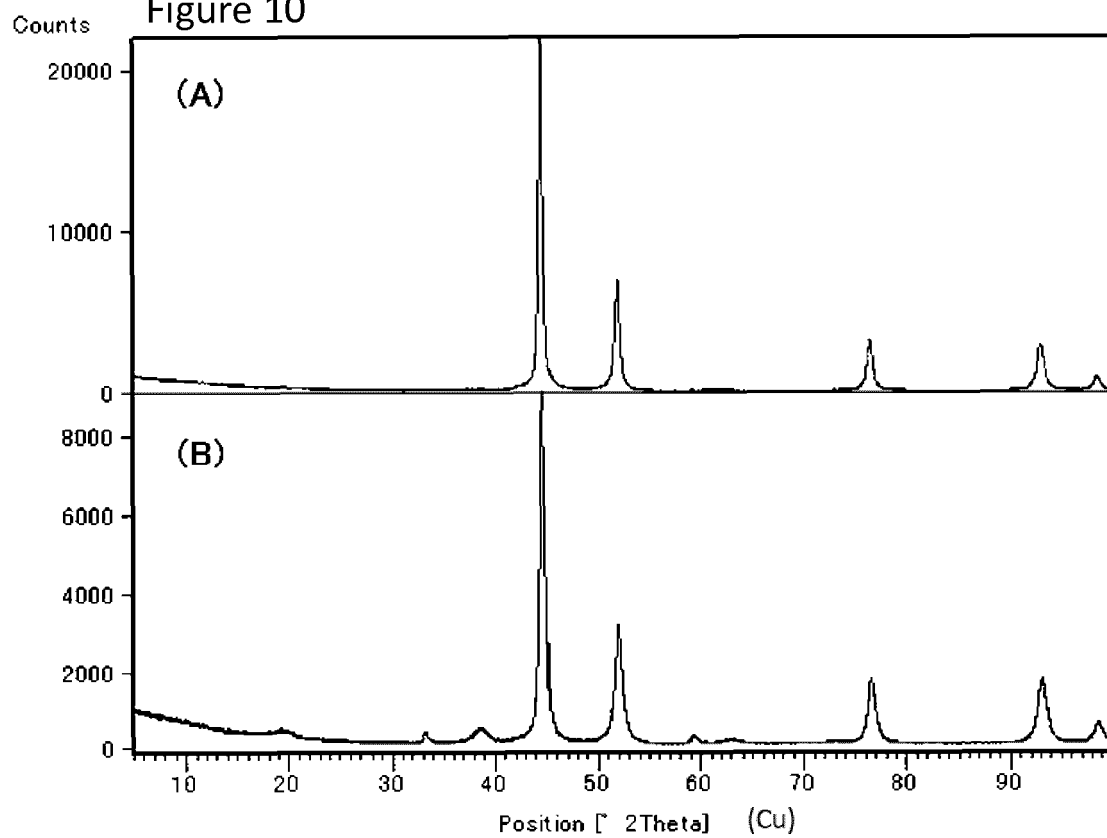


Figure 11

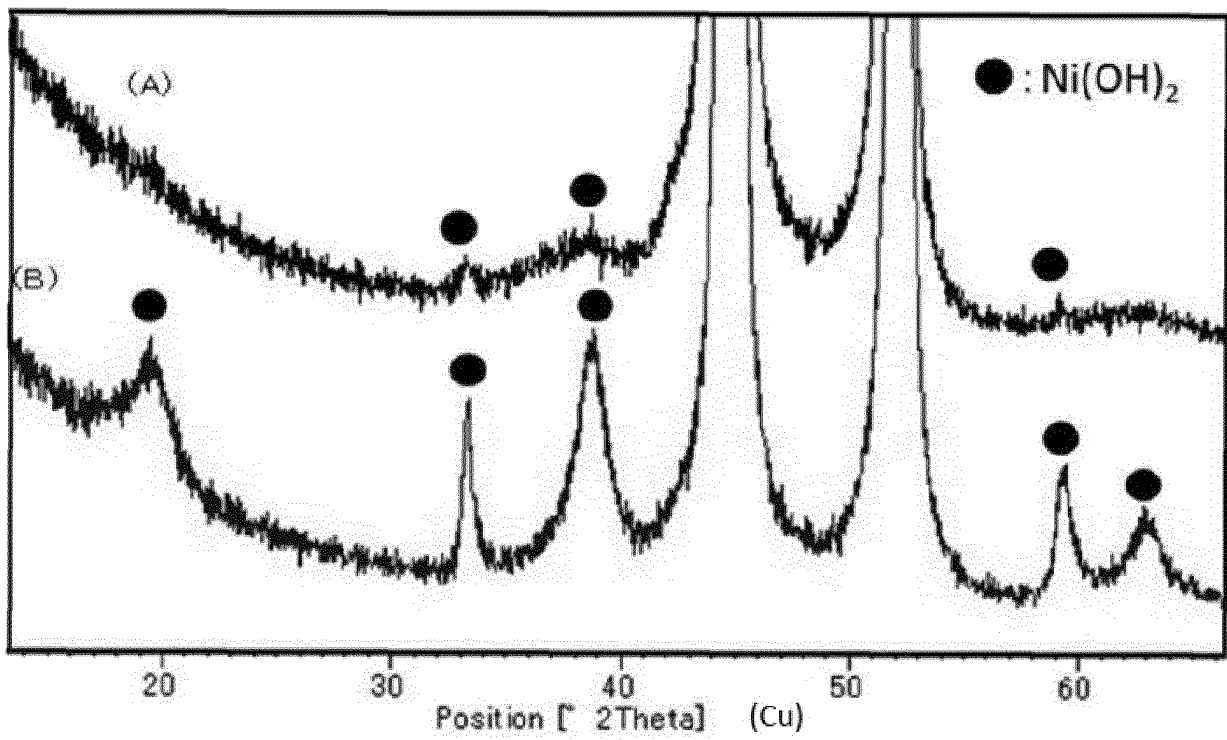
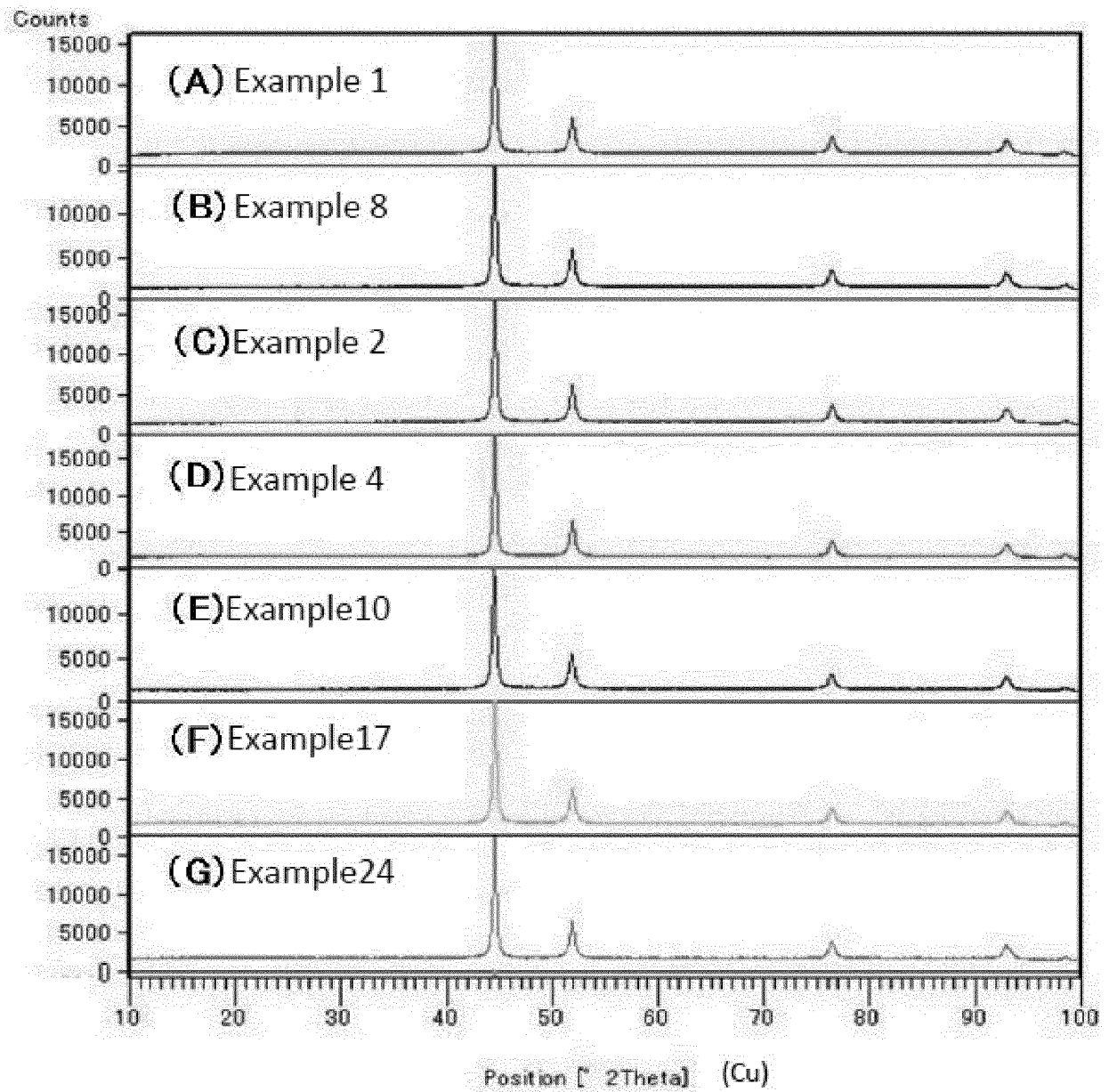


Figure 12



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/064107

A. CLASSIFICATION OF SUBJECT MATTER

B22F1/00(2006.01)i

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)

B22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015
 Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

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.
X Y	JP 2014-162967 A (Nippon Steel & Sumikin Chemical Co., Ltd.), 08 September 2014 (08.09.2014), claims; paragraphs [0064], [0091] to [0092] (Family: none)	12, 13 1-11, 13, 14
Y	JP 2014-173105 A (Nippon Steel & Sumikin Chemical Co., Ltd.), 22 September 2014 (22.09.2014), paragraph [0039] (Family: none)	1-11, 13, 14

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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Date of the actual completion of the international search
07 August 2015 (07.08.15)Date of mailing of the international search report
18 August 2015 (18.08.15)
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 Tokyo 100-8915, Japan

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Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/064107

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	WO 2012/014530 A1 (M Technique Co., Ltd.), 02 February 2012 (02.02.2012), claims (Family: none)	11,13,14
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