(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 559 502 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
20.02.2013 Bulletin 2013/08

(21) Application number: **11768681.6**

(22) Date of filing: **25.02.2011**

(51) Int Cl.:
B22F 1/00 *(2006.01)* ***B22F 9/00*** *(2006.01)*
B22F 9/22 *(2006.01)* ***H01B 1/22*** *(2006.01)*
H01B 5/00 *(2006.01)*

(86) International application number:
PCT/JP2011/055012

(87) International publication number:
WO 2011/129160 (20.10.2011 Gazette 2011/42)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **12.04.2010 JP 2010091360**

(71) Applicant: **JFE Mineral Company, Ltd.**
Minato-ku
Tokyo 105-0014 (JP)

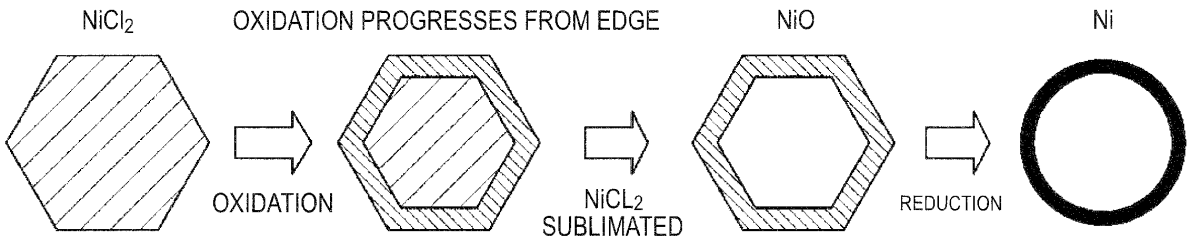
(72) Inventors:
- **MAKISE, Takanori**
  Tokyo 105-0014 (JP)
- **SATO, Nobuyuki**
  Tokyo 105-0014 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) NICKEL FINE PARTICLE, MIXTURE OF NICKEL FINE PARTICLES, CONDUCTIVE PASTE AND METHOD FOR PRODUCING NICKEL FINE PARTICLE

(57) To provide a nickel fine particle which can easily form a conductive path when contained in a conductive paste. A nickel fine particle which is formed of a ring body having a ring shape is formed by oxidizing a nickel chloride fine particle and, thereafter, by reducing a nickel oxide fine particle. By forming the nickel fine particle into the ring body, affinity between the nickel fine particle and a binder resin is improved so that a conductive path can be easily formed.

FIG.1A FIG.1B FIG.1C FIG.1D



EP 2 559 502 A1

Description

[Technical Field]

[0001] The present invention relates to a nickel fine particle, a mixture of nickel fine particles, a conductive paste and a method for producing a nickel fine particle.

[Background Art]

[0002] Conventionally, a metal fine particle is used as a conductive filler contained in a conductive paste, and a nickel fine particle is known as such a metal fine particle. The nickel fine particle has characteristics that although the nickel fine particle has high intrinsic electric resistance compared to a silver fine particle and a copper fine particle, the nickel fine particle does not cause the migration, resists the oxidation relatively strongly and suffers minimally from a change in conductivity over time.

[0003] Various shapes have been considered as a shape of the above-mentioned metal fine particle. For example, although a spherical shape is popular as a shape of the metal fine particle, from a viewpoint of forming a conductive paste into a thin film or the like, it is preferable that the metal fine particle have a thin flaky shape rather than a spherical shape.

[0004] Accordingly, recently, a nickel fine particle having a flaky shape has been developed. For example, patent document 1 discloses a technique where a flaky nickel fine particle is manufactured by reducing a flaky nickel hydroxide particle which is formed by a reaction. Further, patent document 2 discloses a technique where a flaky nickel fine particle is manufactured by plastically deforming a spherical nickel particle mechanically into a flattened shape using a ball mill or the like.

[Prior art document]

[Patent document]

[0005]

[Patent document 1] JP-A-2000-63916
[Patent document 2] JP-A-2005-256039

[Summary of the Invention]

[Task to be solved by the Invention]

[0006] However, the flaky nickel fine particle has the plate-shaped structure having a surface with a certain amount of area and hence, when the nickel fine particles are contained in a conductive paste together with binder resins as conductive fillers, the nickel fine particle exhibits inferior contact performance with the binder resin. Accordingly, in the conductive paste containing the flaky nickel fine particles, the nickel fine particles are liable to coagulate with each other or the binder resins are liable to coagulate with each other thus giving rise to a possibility that a conductive path is obstructed.

Accordingly, it is an object of the present invention to provide a nickel fine particle which can easily form a conductive path when the nickel fine particle is contained in a conductive paste.

[Means for solving the problem]

[0007] The inventors of the present invention have made extensive studies for overcoming the above-mentioned drawbacks and, as a result, have found that by forming a nickel fine particle into a ring body, affinity between the nickel fine particle and a binder resin is improved so that a conductive path is easily formed, and have completed the present invention based on such finding.

That is, the present invention provides the following (1) to (11).

[0008] (1) A nickel fine particle formed of a ring body having a ring shape.

[0009] (2) The nickel fine particle described in the above-mentioned (1), wherein the ring body has a center hole portion and a peripheral portion which surrounds the periphery of the hole portion.

[0010] (3) The nickel fine particle described in the above-mentioned (2), wherein the ring body has a thin plate shape.

[0011] (4) The nickel fine particle described in the above-mentioned (2) or (3), wherein the ring body has, as a part of

the peripheral portion, a breaking portion where the peripheral portion is broken.

[0012] (5) The nickel fine particle described in the above-mentioned (4), wherein the breaking portion occupies 1/2 or less of a volume of the peripheral portion.

[0013] (6) The nickel fine particle described in any one of the above-mentioned (1) to (5), wherein an outer diameter of the ring body is 0.05 to 100 μm.

[0014] (7) A mixture of nickel fine particles which contains the nickel fine particle described in any one of the above-mentioned (1) to (6) and other nickel fine particles.

[0015] (8) A conductive paste which contains at least the nickel fine particle described in any one of the above-mentioned (1) to (6) and a binder resin.

[0016] (9) A method of manufacturing a nickel fine particle, comprising:

changing a nickel chloride phase into a solid phase from a gas phase by cooling a nickel chloride gas, to obtain a nickel chloride fine particle having a thin plate shape;
oxidizing the nickel chloride fine particle to obtain a nickel oxide fine particle; and
reducing the nickel oxide fine particle, thus manufacturing a nickel fine particle which is formed of a ring body having a ring shape.

(10) The method described in the above-mentioned (9), wherein the cooling comprises cooling by an endothermic reaction caused by the oxidation of a solid nickel chloride.

(11) The method described in the above-mentioned (10), wherein the nickel chloride fine particle having a thin plate shape is a nickel chloride fine particle having a hexagonal thin plate shape.

[Advantage of the Invention]

[0017] According to the present invention, it is possible to provide a nickel fine particle which is thin and can make the adhesion between the fine particles difficult.

[Brief Description of the Drawings]

[0018]

Fig. 1 is a schematic view showing a formation mechanism of a nickel fine particle according to the present invention.
Fig. 2 is a cross-sectional view schematically showing a reaction device 101.
Fig. 3 is an SEM photograph obtained by photographing a nickel fine particle.
Fig. 4 is an SEM photograph obtained by photographing a nickel fine particle.
Fig. 5 is an SEM photograph obtained by photographing a nickel fine particle.
Fig. 6 is an SEM photograph obtained by photographing a nickel oxide fine particle.

[Mode for Carrying out the Invention]

[0019] A nickel fine particle according to the present invention is a nickel fine particle formed of a ring body having a ring shape.
The nickel fine particle according to the present invention, in summary, is formed by oxidizing a nickel chloride ($NiCl_2$) fine particle and, thereafter, by reducing the fine particle.
Hereinafter, a mechanism that the nickel fine particle according to the present invention is formed is explained in conjunction with Fig. 1. Fig. 1 is a schematic view showing the formation mechanism of the nickel fine particle according to the present invention.

[0020] Firstly, the nickel chloride fine particle is explained. As shown in Fig. 1(A), the nickel chloride fine particle is a crystal having a hexagonal thin plate shape. This is because the crystal is liable to grow in the longitudinal direction of the plate.

[0021] Although a nickel chloride fine particle may be obtained by directly charging a raw material into a reaction system, it is preferable to obtain the nickel chloride fine particle by changing a nickel chloride phase into a solid phase from a gas phase by cooling a nickel chloride gas in a reaction system. In this case, a size of the obtained fine particle can be controlled based on conditions at the time of changing the phase of the nickel chloride into a solid phase from a gas phase.

[0022] As a method of obtaining a nickel chloride gas, for example, a method which sublimates solid nickel chloride, a method which blows a chlorine gas into heated metal nickel or the like is named. However, in view of a fact that a chlorine gas corrodes metal thus making handling of the chlorine gas difficult, it is preferable to adopt the method which

obtains the nickel chloride gas by sublimating solid nickel chloride.

Although a temperature at which solid nickel chloride is sublimated may preferably be set to a high temperature for increasing an amount of sublimation, there is an upper limit with respect to a temperature at which an inexpensive exothermic body can be used and hence, it is preferable to set the temperature to 900 to 1200°C.

[0023] Next, a nickel oxide fine particle is obtained by oxidizing the nickel chloride fine particle. Here, the more unstable a surface of the nickel chloride fine particle becomes, the more crystals are liable to grow on the surface so that a reaction is liable to be caused on a longitudinal surface of the plate. Therefore, the oxidization of the nickel chloride fine particle having a hexagonal shape progresses toward the center from an edge as shown in Fig. 1(B).

Here, the oxidization is finished before the nickel chloride fine particle is completely oxidized and hence, as shown in Fig. 1(B), a state where only an outer peripheral portion of the nickel chloride fine particle is oxidized is brought about. Thereafter, by sublimating a nickel chloride portion remaining in the center portion, as shown in Fig. 1 (C), a ring-shaped nickel oxide (NiO) fine particle is obtained.

[0024] As an oxidizing agent used in oxidizing the nickel chloride fine particle, for example, water vapor, oxygen, sulfur dioxide or the like is named. In view of easy handling with no toxicity, water vapor is preferable.

When nickel chloride is oxidized by reacting with water vapor, a reaction expressed by the following formula (I) progresses.

$$NiCl_2 + H_2O \rightarrow NiO + 2HCl \qquad (I)$$

[0025] Next, as shown in Fig. 1 (D), by reducing the nickel oxide fine particle having a ring shape, the nickel fine particle according to the present invention is obtained in a state where a ring shape of the nickel oxide fine particle is maintained as it is. That is, the nickel fine particle according to the present invention is formed of a ring body having a ring shape.

Here, in view of the formation of the fine line structure, it is preferable to set an outer diameter of the ring body as small as possible. However, when the outer diameter of the ring body is excessively small, the coagulation between the nickel fine particles is strengthened. Accordingly, it is preferable to set the outer diameter of the ring body to 0.05 to 100 μm, and it is more preferable to set the outer diameter of the ring body to 0.5 to 10 μm. It is preferable to set a plate thickness of the ring body to 0.01 to 10 μm.

Control of outer diameter of ring:

[0026] A size of the ring depends on a size of a planar particle of nickel chloride formed by sublimation. Accordingly, along with the increase in a size of the nickel chloride particle brought about by the prolongation of the time the nickel chloride stays in a sublimation portion, the ring having a larger outer diameter is formed.

Control of inner diameter of ring:

[0027] An outer peripheral portion of the planar nickel chloride is constituted of a surface having high interfacial surface energy and hence, a reaction is liable to occur on the outer peripheral portion. Accordingly, when the nickel chloride particle is oxidized, the oxidization occurs from the outer peripheral portion. The longer a time for oxidizing the formed nickel chloride particle, the more the oxidization progresses so that a size of an inner hole is decreased. Further, a reaction speed also influences the control of an inner diameter of the ring, and it is possible to make the reaction progress faster corresponding to the elevation of temperature within a temperature range where nickel chloride is not sublimated. Still further, the higher the oxygen concentration, the faster the reaction progresses. By making the reaction progress faster, it is possible to acquire an advantageous effect substantially equal to an advantageous effect which is acquired by prolonging a reaction time.

[0028] As a reducing agent used in reducing the nickel oxide fine particle, for example, hydrogen, magnesium or the like is named. However, in view of a reason that magnesium is liable to form an alloy thereof, hydrogen is preferably used. In reducing nickel oxide using hydrogen, a reaction expressed by the following formula (II) progresses.

$$NiO+H_2 \rightarrow Ni+H_2O \qquad (II)$$

[0029] When the oxidization of the ring-shaped nickel oxide fine particle is insufficient so that the nickel chloride partially remains in the nickel oxide fine particle, a volume of the fine particle is largely decreased when nickel chloride is reduced to nickel and hence, the ring body is broken into pieces at the time of reduction and thereby string-shaped nickel fine particles are formed.

[0030] Although the mechanism that the nickel fine particle according to the present invention is formed has been explained heretofore, in the present invention, it is preferable to reduce a reduction product using hydrogen after a nickel chloride gas is made to react with water vapor.

Here, firstly, due to a reaction between the nickel chloride gas and water vapor, solid nickel oxide is formed. Since this reaction is an exothermic reaction, the remaining nickel chloride gas not used in the reaction is cooled so that a nickel chloride phase is changed into a solid phase from a gas phase and thereby a nickel chloride fine particle having a hexagonal thin plate shape is formed.

With respect to the nickel chloride fine particle having a hexagonal thin plate shape formed in this manner, due to a reaction between the nickel chloride fine particle and water vapor which is not used in the above-mentioned reaction, only an outer peripheral portion of the fine particle is oxidized and a center portion of the fine particle is sublimated and thereby a ring-shaped nickel oxide fine particle according to the present invention is obtained. Thereafter, the ring-shaped nickel oxide fine particle according to the present invention is reduced using hydrogen so that the nickel fine particle according to the present invention is formed.

Nickel chloride sublimated from the center portion of the nickel chloride fine particle having a hexagonal thin plate shape also reacts with water vapor not used in the above-mentioned reaction so that nickel oxide which differs from the ring-shaped nickel oxide fine particle according to the present invention is formed. This reaction is also an exothermic reaction, and also due to this exothermic reaction, a nickel chloride gas is cooled so that a nickel chloride phase is changed into a solid phase from a gas phase and thereby a nickel chloride fine particle having a hexagonal thin plate shape is formed.

[0031] As described above, in reducing a reaction product using hydrogen after making a nickel chloride gas react with water vapor, it is preferable to supply 1 to 10 mol of water vapor with respect to 1 mol of nickel chloride gas, and it is more preferable to supply 2 to 7 mol of water vapor with respect to 1 mol of nickel chloride gas. Further, it is preferable to supply 1 to 5 mol of hydrogen with respect to 1 mol of nickel chloride gas, and it is more preferable to supply 2 to 4 mol of hydrogen with respect to 1 mol of nickel chloride gas.

By setting a supply amount of water vapor and a supply amount of hydrogen within the above-mentioned ranges, not only a flaky and string-shaped nickel fine particle but also a ring-shaped nickel fine particle are formed.

[0032] The nickel fine particle according to the present invention is formed of the ring body as described above, and the ring body has a center hole portion and a peripheral portion which surrounds the periphery of the hole portion.

Fig. 3 is an SEM photograph obtained by photographing a nickel fine particle. Examples which clearly show a ring-body shape of the nickel fine particle according to the present invention are ring bodies indicated by A to D in the SEM photograph shown in Fig. 3. Although all ring bodies A through D are included in the category of the nickel fine particle according to the present invention, the present invention is not limited to such ring bodies.

[0033] The ring body A is a typical example where a shape of the nickel chloride fine particle which is a hexagonal thin plate shape is held. That is, the ring body A is formed into a thin plate shape and includes a hexagonal peripheral portion and a circular hole portion.

[0034] The ring body B is also an example where the ring body B is formed into a thin plate shape in the same manner as the ring body A, and includes a hexagonal peripheral portion and a circular hole portion. However, a diameter of the hole portion of the ring body B is set smaller than a diameter of the hole portion of the ring body A.

[0035] The ring body C has a thin plate shape and, also includes a hexagonal peripheral portion and a circular hole portion. However, a part of the peripheral portion is broken. That is, the ring body C includes a breaking portion where the peripheral portion is broken, and the breaking portion forms a part of the peripheral portion in the present invention. In the ring body C, the breaking portion occupies approximately 1/6 of a volume of the peripheral portion. Further, in the ring body D, a breaking portion occupies an amount slightly smaller than 1/2 of a volume of a peripheral portion. It is considered that this breaking portion is formed in the course of the manufacture of a nickel fine particle.

[0036] The ring body such as the above-mentioned ring body A, for example, has a minimum outer diameter and a maximum outer diameter in the plate surface direction. When the ring body holds a hexagonal shape, a ratio between the minimum outer diameter and the maximum outer diameter (minimum outer diameter/ maximum outer diameter) theoretically becomes $\sqrt{3}/2$ (8.66/10). Even when a hexagonal shape is held insufficiently, it is preferable to set the ratio to 1/10 or more, and it is more preferable to set the ratio to 2/10 or more.

It is also preferable to set a ratio between a plate thickness and a maximum outer diameter (plate thickness/maximum outer diameter) to 1/100 to 10/100.

Further, in viewing the ring body such as the ring body A described above, for example, in the direction perpendicular to a plate surface, it is preferable to set an area ratio between the peripheral portion and the hole portion (peripheral portion/ hole portion) to 1/1 to 1/1000.

Provided that a shape and a size of the nickel fine particle according to the present invention fall within the above-mentioned ranges, the nickel fine particle exhibits excellent affinity with a binder resin.

[0037] Fig. 4 and Fig. 5 show SEM photographs obtained by photographing nickel fine particles. However, Fig. 4 and Fig. 5 show the SEM photographs obtained by photographing the nickel fine particles which are formed by methods different from the above-mentioned method.

The nickel fine particle which the SEM photograph shown in Fig. 4 indicates is a nickel fine particle which was manufactured by excessively oxidizing a nickel chloride fine particle having a hexagonal thin plate shape. In this case, as shown in Fig. 4, although a flaky nickel fine particle was confirmed, a ring body was not confirmed. The nickel fine particle which

the SEM photograph shown in Fig. 5 indicates is a nickel fine particle which was manufactured by insufficiently oxidizing a nickel chloride fine particle having a hexagonal thin plate shape. In this case, as shown in Fig. 5, a ring body was not confirmed, and string-shaped nickel was confirmed.

[0038] Next, a mixture of nickel fine particles according to the present invention is explained. The mixture of nickel fine particles according to the present invention is a mixture of nickel fine particles which contains a nickel fine particle according to the present invention and other nickel fine particles.

In the SEM photograph shown in Fig. 3, other nickel fine particles are also included besides the nickel fine particle according to the present invention and hence, it is safe to say that the SEM photograph shown in Fig. 3 indicates the mixture of nickel fine particles according to the present invention.

In the mixture of nickel fine particles according to the present invention, it is preferable that a mass ratio between the nickel fine particle according to the present invention and other nickel fine particles (nickel fine particle according to the present invention/other nickel fine particles) is above 1/1. By setting the mass ratio to such a value, the mixture of nickel fine particles exhibits excellent affinity with a binder resin so that a conductive path can be easily formed.

[0039] Next, a conductive paste according to the present invention is explained. The conductive paste according to the present invention is a metal paste which contains at least a nickel fine particle according to the present invention and a binder resin. The conductive paste according to the present invention contains the nickel fine particle according to the present invention and hence, a conductive path can be easily formed and thereby the conductive paste exhibits excellent conductivity.

[0040] The conductive paste according to the present invention may contain a solvent, various additives and the like when necessary.

A method of manufacturing the conductive paste according to the present invention is not particularly limited and, for example, a method which mixes nickel powder according to the present invention, a binder resin, a solvent, various additives and the like together using a kneader, a roll or the like is named.

[Examples]

[0041] Hereinafter, the present invention is specifically explained by listing examples. However, the present invention is not limited to these examples.

In examples and reference examples explained hereinafter, a reaction device 101 shown in Fig. 2 was used. Fig. 2 is a cross-sectional view schematically showing the reaction device 101. A nickel fine particle was manufactured by causing a reaction in the inside of a quartz tube 103 having an inner diameter of 46 mmϕ which the reaction device 101 includes. A horizontal furnace 102 which covers the quartz tube 103 (and a portion of the quartz tube 103 which the horizontal furnace 102 covers) is divided into three zones (a zone 1, a zone 2 and a zone 3), and predetermined temperatures in the respective zones were made different from each other depending on cases.

A nitrogen (N_2) gas which is a carrier gas was supplied to the quartz tube 103 at a rate of 6.5Nl/min. Further, a quartz-made nozzle 104 was arranged in the inside of the quartz tube 103, and a hydrogen (H_2) gas was supplied to the zone 3 in the inside of the quartz tube 103 at a rate of 3Nl/min. A nickel-made crucible 111 in which water is stored was arranged in the zone 1 in the inside of the quartz tube 103, and the water was vaporized. A crucible made of nickel 112 in which solid nickel chloride (purity: 99.9%, made by Wako Pure Chemical Industries, Ltd.) is stored was arranged in the zone 2 in the quartz tube 103, and the solid nickel chloride was sublimated. A collector (not shown in the drawing) was arranged at a terminal end of the quartz tube 103. A glass fiber filter (made by Advantec Co., Ltd.) was used as the collector. A nitrogen (N_2) gas for cooling is supplied to an area in the vicinity of the terminal end in the inside of the quartz tube 103.

[0042] In the zone 2 in the inside of the quartz tube 103, due to cooling generated by a reaction between sublimated nickel chloride and water vapor which is vaporized water (exothermic reaction), a nickel chloride fine particle having a hexagonal thin plate shape was formed from the sublimated nickel chloride, and a nickel oxide fine particle was formed by causing a reaction between the nickel chloride fine particle and water vapor. Then, in the zone 3, the nickel oxide fine particle was reduced by causing a reaction between the nickel oxide fine particle and hydrogen thus forming a nickel fine particle.

<Example 1>

[0043] The predetermined temperature in the horizontal furnace 102 was set such that the temperature in the zone 1 was 1000°C, the temperature in the zone 2 was 1000°C and the temperature in the zone 3 was 980°C. The crucible 111 storing 10g of water and the crucible 112 storing 40g of solid nickel chloride were arranged in the lateral furnace 102. A carrier gas and a hydrogen gas were supplied to the horizontal furnace 102 under the above-mentioned conditions, and a reaction time was set to 10 minutes.

[0044] In the example 1, 3 mol of water vapor and 3 mol of hydrogen were supplied with respect to 1 mol of sublimed

nickel chloride. An amount of sublimation of nickel chloride was determined by detecting a hydrogen chloride gas which was generated due to a reaction of nickel chloride with hydrogen, and an amount of vaporization was calculated based on a vaporization time with respect to water vapor (the substantially same steps being taken in the following example).

[0045] A nickel fine particle which is a reaction product was collected by a collector, and the nickel fine particle was observed using a scanning electron microscope (SEM) (S-4300 made by Hitachi High Technologies Corporation., the substantially same step being taken in the following example). Here, the above-mentioned Fig. 3 shows the SEM photograph obtained by photographing the nickel fine particle which is the reaction product in the example 1. As shown in Fig. 3, in the example 1, a nickel fine particle which is a ring body was confirmed.

<Reference example 1>

[0046] The substantially same steps as the example 1 were carried out except for that a hydrogen gas was not supplied to the inside of the quartz tube 103 from the nozzle 104.

In the reference example 1, when a reaction product was observed using the SEM, a ring body was confirmed also in the reference example 1.

Then, when an analysis using an EDX (energy-dispersion-type X-ray analyzer) attached to the SEM was done with respect to the same portion in the SEM photograph shown in Fig. 6, nickel was 56 mol% and O was 44 mol% (Ni:O $\approx$ 1: 1). From this result, it is understood that a ring-shaped nickel oxide fine particle was collected as a reaction product in the reference example 1. That is, Fig. 6 shows an SEM photograph obtained by photographing a nickel oxide fine particle.

From the reference example 1, it is understood that a ring body was already formed before the hydrogen reduction was performed in the zone 3 in the inside of the quartz tube 103 according to the above-mentioned example 1.

[Description of Reference Numerals and Signs]

[0047]

101: reaction device
102: horizontal furnace
103: quartz tube
104: nozzle
111: crucible
112: crucible

Claims

1. A nickel fine particle formed of a ring body having a ring shape.

2. The nickel fine particle according to claim 1, wherein the ring body has a center hole portion and a peripheral portion which surrounds the periphery of the hole portion.

3. The nickel fine particle according to claim 2, wherein the ring body has a thin plate shape.

4. The nickel fine particle according to claim 2 or 3, wherein the ring body has, as a part of the peripheral portion, a breaking portion where the peripheral portion is broken.

5. The nickel fine particle according to claim 4, wherein the breaking portion occupies 1/2 or less of a volume of the peripheral portion.

6. The nickel fine particle according to any one of claims 1 to 5, wherein an outer diameter of the ring body is 0.05 to 100 μm.

7. A mixture of nickel fine particles which contains the nickel fine particle described in any one of the claims 1 to 6 and other nickel fine particles.

8. A conductive paste which contains at least the nickel fine particle described in any one of claims 1 to 6 and a binder resin.

9. A method of manufacturing a nickel fine particle, comprising:

changing a nickel chloride phase into a solid phase from a gas phase by cooling a nickel chloride gas, to obtain a nickel chloride fine particle having a thin plate shape;
oxidizing the nickel chloride fine particle to obtain a nickel oxide fine particle; and
reducing the nickel oxide fine particle, thus manufacturing a nickel fine particle which is formed of a ring body having a ring shape.

10. The method according to claim 9, wherein the cooling comprises cooling by an endothermic reaction caused by the oxidation of a solid nickel chloride.

11. The method according to claim 10, wherein the nickel chloride fine particle having a thin plate shape is a nickel chloride fine particle having a hexagonal thin plate shape.

FIG.1A

FIG.1B

FIG.1C

FIG.1D

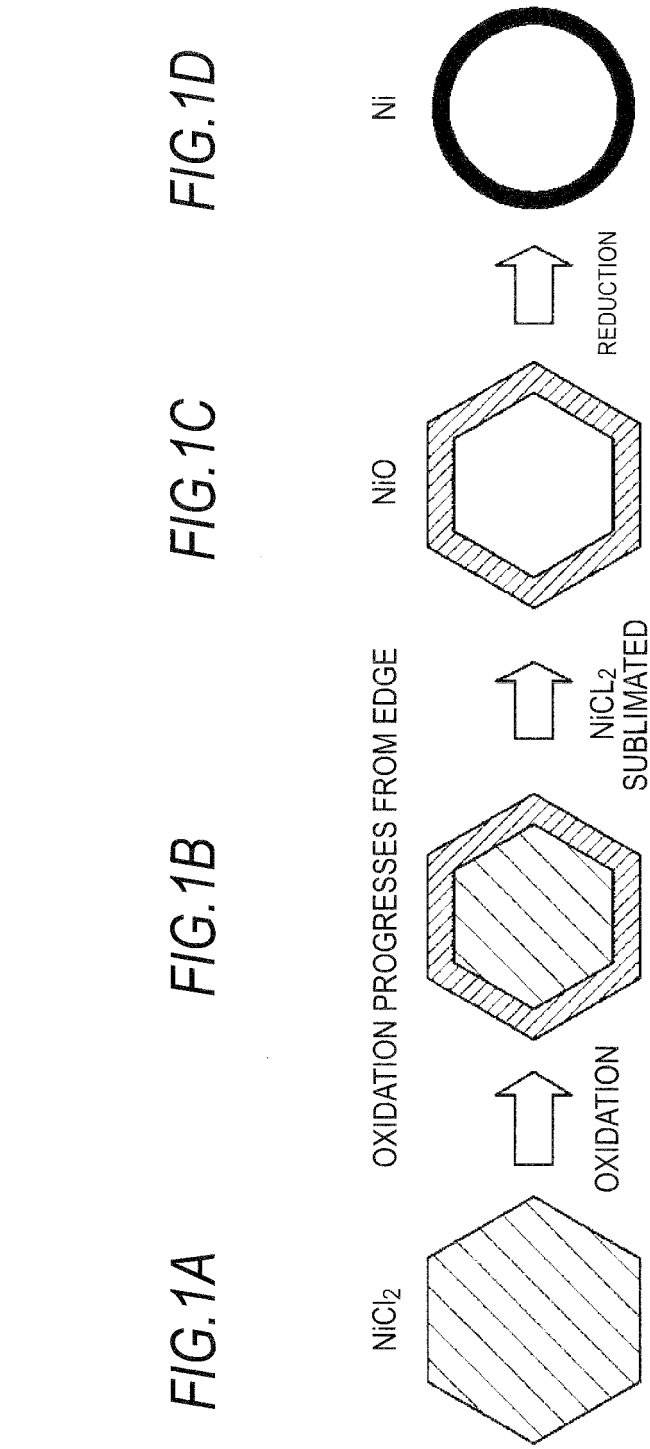


FIG.2

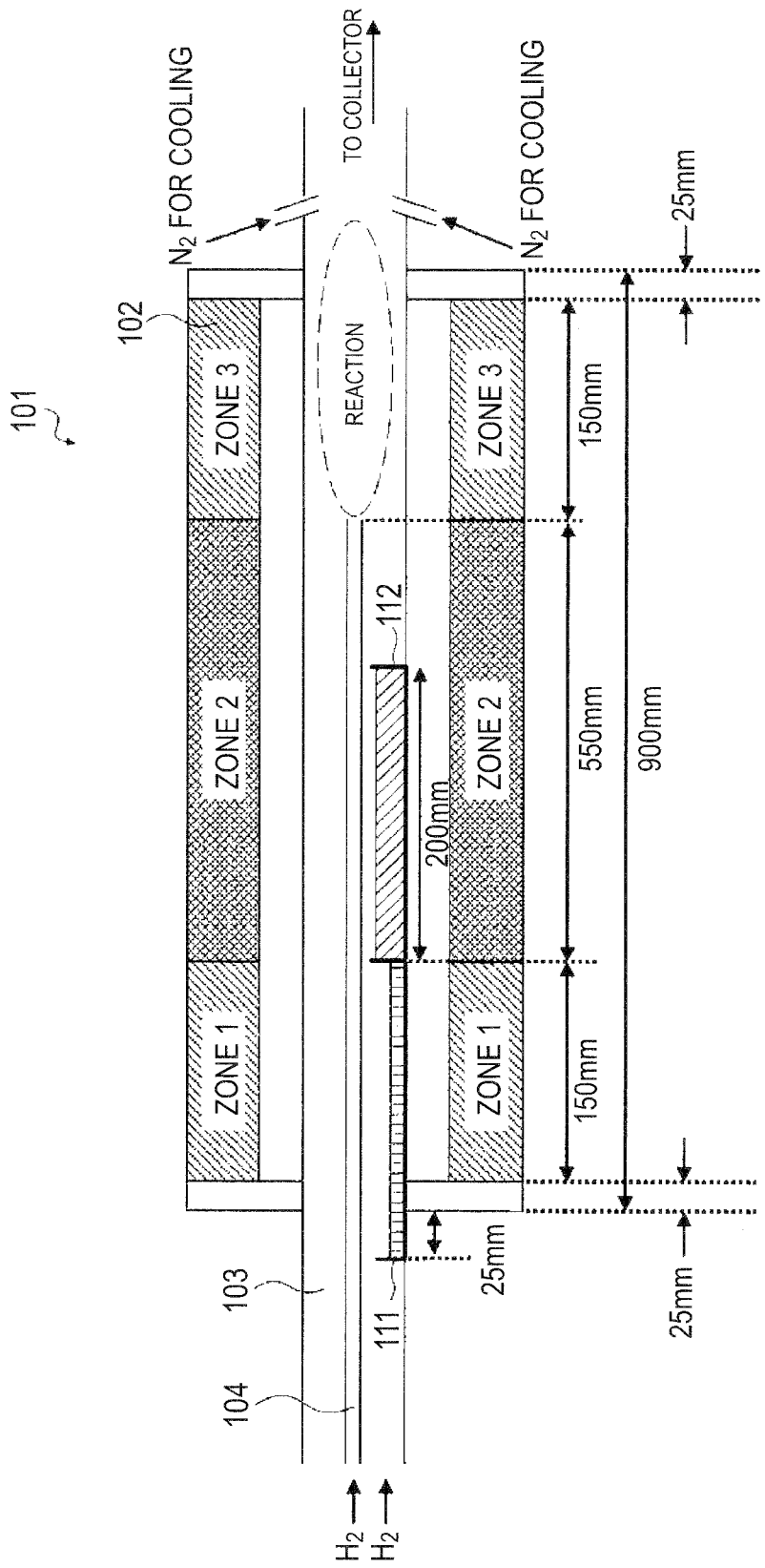

101
102
N_2 FOR COOLING
TO COLLECTOR
N_2 FOR COOLING
25mm
ZONE 3
REACTION
ZONE 3
150mm
112
ZONE 2
200mm
ZONE 2
550mm
900mm
ZONE 1
150mm
ZONE 1
103
111
25mm
25mm
104
H_2
H_2

FIG.3

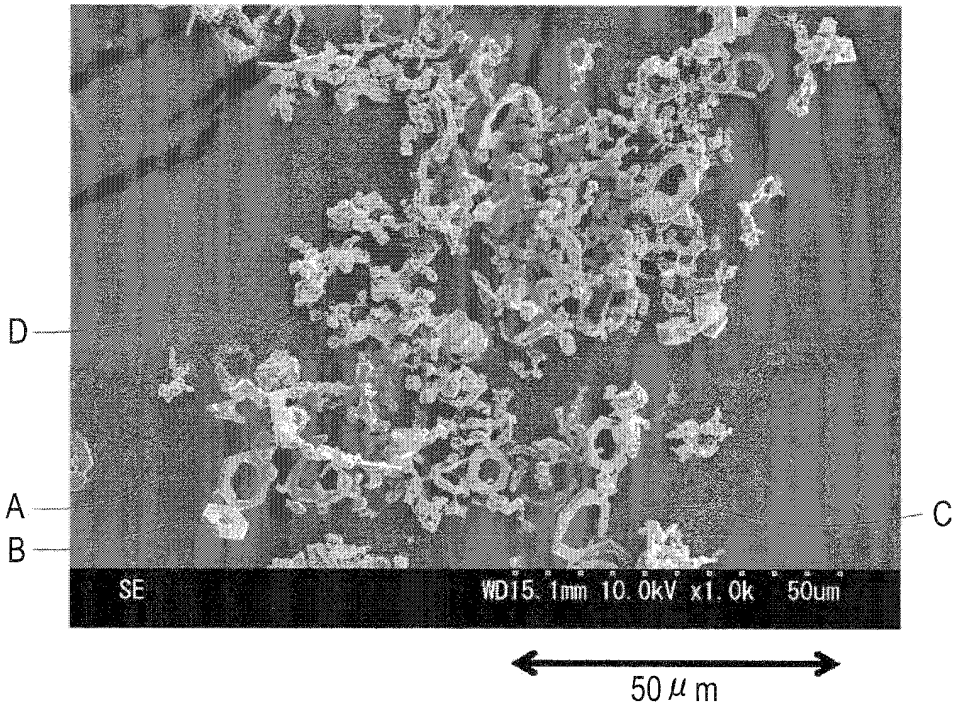

D
A
B
C
SE
WD15.1mm 10.0kV x1.0k 50um
50 μm

FIG.4

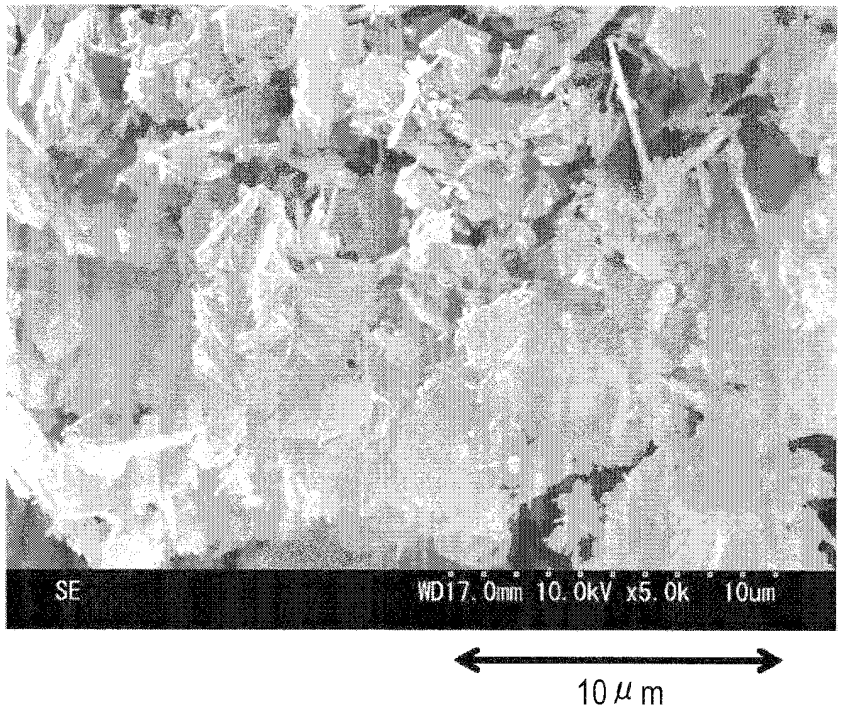

SE
WD17.0mm 10.0kV x5.0k 10um
10 μm

FIG.5

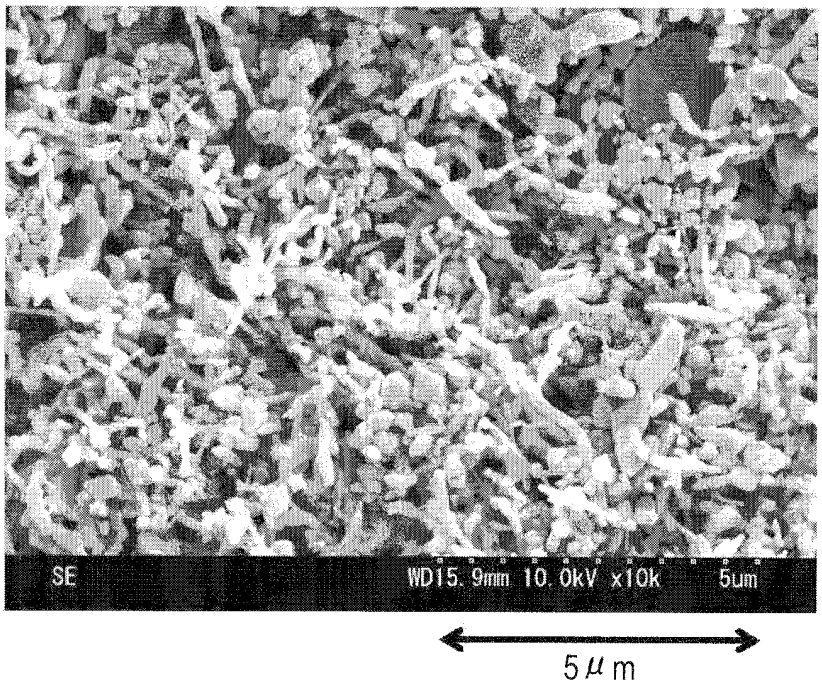
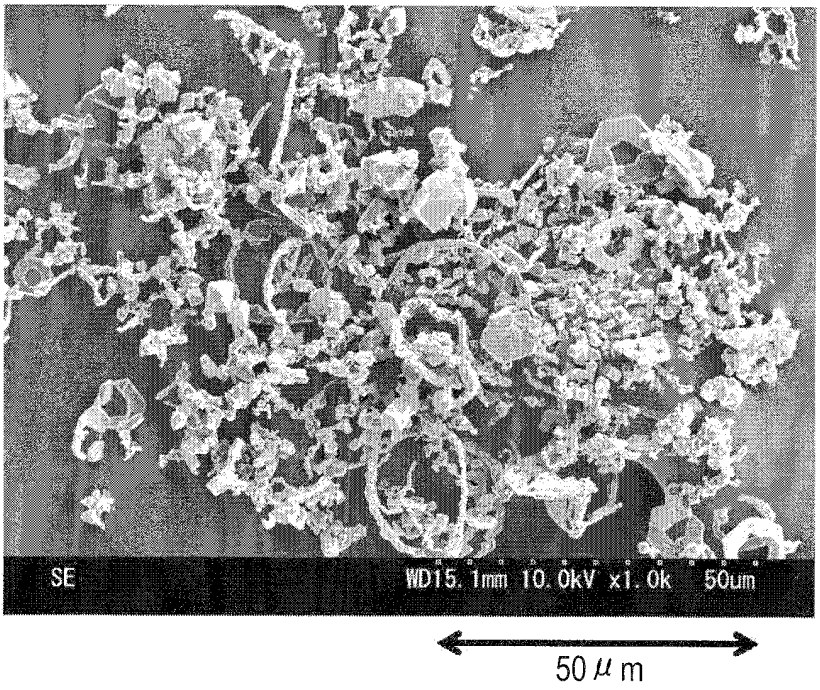

SE
WD15.9mm 10.0kV x10k 5um
5 μ m

FIG.6


SE
WD15.1mm 10.0kV x1.0k 50um
50 μ m

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/055012

A. CLASSIFICATION OF SUBJECT MATTER
B22F1/00(2006.01)i, *B22F9/00*(2006.01)i, *B22F9/22*(2006.01)i, *H01B1/22*(2006.01)i, *H01B5/00*(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, B22F9/00, B22F9/22, H01B1/22, H01B5/00

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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.
A	JP 2000-234109 A (Sumitomo Metal Mining Co., Ltd.), 29 August 2000 (29.08.2000), claims (Family: none)	1-11
A	JP 2000-336408 A (Sumitomo Metal Mining Co., Ltd.), 05 December 2000 (05.12.2000), claims (Family: none)	1-11

☐ 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
23 May, 2011 (23.05.11)	31 May, 2011 (31.05.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2000063916 A **[0005]**
- JP 2005256039 A **[0005]**