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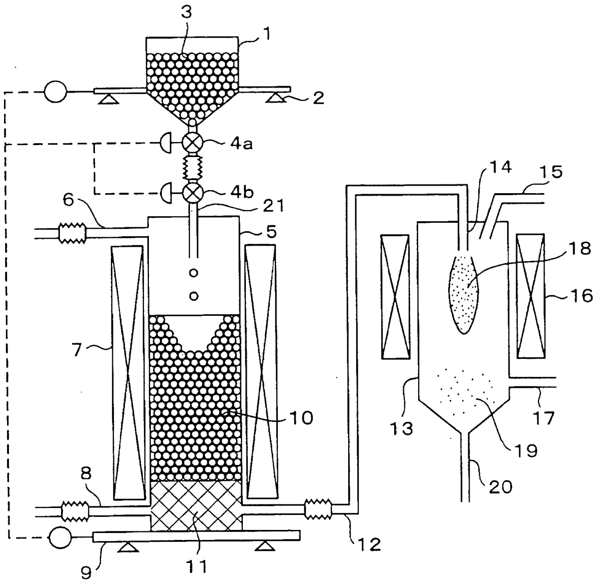
(54) METHOD AND DEVICE FOR PRODUCING METAL POWDER

(57) Raw metal is intermittently and continuously charged into a chlorination furnace, the raw metal and chlorine gas are reacted in the chlorination furnace to continuously generate metal chloride vapor, and the metal chloride vapor and hydrogen gas are reacted in a reduction furnace to continuously obtain metallic powder. Furthermore, the chlorination furnace in which the chlorination reaction is proceeding is weighed, and the charged amount of the raw metal to the chlorination furnace is controlled depending on the weighing result.

Fig. 1



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Description

Technical Field

[0001] The present invention relates to a method for production of metallic powder and to a production device for the metallic powder, and in particular, relates to a method for production of a metallic powder and to a production device for the metallic powder, such as one of nickel, which is appropriate for various purposes such as for conductive paste filler used in electronic parts such as multilayer ceramic capacitors or the like, bonding materials for titanium materials, or catalysts.

Background Art

[0002] Metallic powders of nickel, copper, or the like are widely used in various fields such as those of electronic materials and catalysts. In recent years, metallic powders which are called "ultrafine particles" having average diameters of not more than 1 µm, have attracted attention as materials for forming internal electrodes used in multilayer ceramic capacitors. Conventionally, noble metal powders such as those of silver, palladium, platinum, and gold, or base metal powders such as those of nickel, cobalt, iron, molybdenum, and tungsten, are used in conductive pastes for electronic materials, and in particular, in internal electrodes of multilayered ceramic capacitors. Generally, a multilayer ceramic capacitor is made by alternately laminating ceramic dielectric layers and metallic layers which are used as internal electrodes, and by forming external electrodes which are connected to the metallic layer of internal electrodes on both faces of the ceramic dielectric layers. Materials which contain a high dielectric constant material as a main component, such as barium titanate, strontium titanate, and yttrium oxide, are used in the dielectric substances. On the other hand, the noble metal powders or base metal powders mentioned above are used as metals which form the internal electrodes. However, since recently more inexpensive electrical materials are required, multilayer ceramic capacitors in which the latter base metal powders are used have been greatly developed. In particular, nickel powder has been mainly developed.

[0003] A multilayer ceramic capacitor may be made by the following method. First, a dielectric powder such as barium titanate is mixed with an organic binder so as to form a suspension. Next, the suspension is formed into a sheet by a doctor blade method to form a dielectric green sheet. In addition, metallic powder for an internal electrode is mixed with an organic compound such as an organic solvent, plasticizer, or organic binder to form a metallic powder paste, and this paste is coated on the green sheet mentioned above by screen printing. After several hundreds of layers thereof are laminated, they are sintered at not less than 1000°C, and then outer electrodes are baked on both sides of the dielectric ceramic layer to obtain a multilayer ceramic capacitor.

[0004] In an organic component removing process in which organic components are vaporized from metallic paste or a sintering process after the removing process in the production of the multilayer ceramic capacitor described above, volume change occurs due to expansion or shrinkage of the metallic powder. On the other hand, similarly, volume change of the dielectric material itself also occurs by sintering. That is to say, since dielectric materials and metallic powders, which are different materials, are sintered at the same time, differences in sintering behavior originating due to volume changes such as expansion or shrinkage of each material cannot be avoided, and as a result, there have been problems such as destruction of layered structure, and so called delamination including, for example, cracking or separation.

[0005] Furthermore, as the size of a capacitor is reduced and capacity of the capacitor increases, not only ultrafine particles having diameters of not more than 1 µm, but also ultrafine particles having diameters of not more than 0.5 µm are required as metallic powders used in internal electrodes so as to increase the number of laminations, by reducing the thicknesses of layers of internal electrodes, and thereby reduce the resistance. At this time, the existence of coarse particles having diameter of not less than 1 µm or 2 µm blocks reduction in the thicknesses of the layers of the internal electrodes. Furthermore, occurrence of uneven parts on the surface of the electrodes causes short of circuiting, and results in delamination.

[0006] A method for production of metallic powder in which few such coarse particles are contained is disclosed in Japanese Unexamined Patent Application Publication No. 98-219313. In this method, a chlorination process in which chlorine gas is contacted to metal to generate metal chloride vapor continuously and a reduction process in which the metal chloride vapor generated in the chlorination process is contacted with reducing gas to reduce the metal chloride continuously are included.

[0007] The method for the production mentioned above is an efficient method because nickel powders, particularly having diameters of not more than 1 µm, can be produced reliably and efficiently. However, coarse particles having diameters of not less than 1 µm or 2 µm are contained in the yielded metallic powder. A method for production or a method for improvement of the device which can reduce generation of coarse particles are required.

Disclosure of the Invention

[0008] Therefore, in a method in which raw metal and chlorine gas are reacted to generate metal chloride vapor, and the metal chloride vapor and hydrogen gas are reacted to obtain metallic powers, an object of the present invention is to provide a method for production and a production device which can produce metallic powders particularly having reliable average diameters of not more than 1 μm appropriate for internal electrodes in multilayer ceramic capacitors, without generating coarse particles.

[0009] The inventors have researched to achieve the object mentioned above and have found that when chlorine gas which is not reacted yet in a chlorination furnace is charged into a reduction furnace, this causes the reaction temperature to increase and generates coarse particles.

[0010] The method for production of metallic powder of the present invention was performed based on the information described above. A method for production of metallic powder comprises: charging raw metal into a chlorination furnace intermittently or continuously; reacting the raw metal and chlorine gas in the chlorination furnace to generate metal chloride vapor continuously; and reacting the metal chloride vapor and hydrogen gas in a reduction furnace to obtain metallic powder continuously and is characterized in weighing the weight of the chlorination furnace in which chlorination reaction is proceeding, and controlling the charged amount of the raw metal into the chlorination furnace depending on the weighing result.

[0011] Furthermore, a production device for the metallic powder of the present invention is characterized in that the device has a raw material hopper to charge raw metal, a chlorination furnace to chlorinate the raw metal charged from the raw material hopper, and a reduction furnace to reduce metal chloride vapor generated in the chlorination furnace, wherein the raw material hopper and the chlorination furnace are communicated with a raw material charging pipe which charges the raw metal via a carrying valve for controlling charged amount thereof, the chlorination furnace and the reduction furnace are communicated with a carrying pipe which carries metal chloride vapor generated in the chlorination furnace to the reduction furnace, the chlorination furnace has a chlorine gas charging pipe to charge chlorine gas inside, the reduction furnace has a nozzle to inject the metal chloride vapor inside; a hydrogen gas charging pipe to charge hydrogen gas inside; and a cooling gas charging pipe to charge inert gas for cooling the reduced metallic powder inside, the production device of the metallic powder further has a weighing means to weigh the entire weight of the chlorination furnace and a controlling means to control the amount of the raw metal charged into the chlorination furnace depending on the weighing result of the weighing method.

[0012] In the present invention, since the charged amount of the raw metal is controlled depending on the measuring result of the weight of the entirety of the chlorination furnace, appropriate amount of raw metal can be always filled in the chlorination furnace. Therefore, the raw metal and the chlorine gas can be reacted uniformly, and it becomes possible to reduce the charged amount of chlorine gas which is not reacted yet.

[0013] As a metallic powder of the present invention, one of a metal which can be used in an internal electrode or a catalyst of multilayer ceramic capacitors can be used. For example, a noble metal such as silver, palladium, platinum, gold or the like, or a base metal such as nickel, cobalt, iron, molybdenum, tungsten or the like. Among these metals, base metals are desirable from the viewpoint of cost, and in particular, nickel is more desirable.

[0014] Although characteristics of particles of the metallic powder produced in the present invention are not particularly limited as long as there is no difficulty in use of each, average diameter of the metallic powder is desirably in a range from 0.01 to 1 μm, more desirably in a range from 0.1 to 1 μm, and further desirably in a range from 0.1 to 0.5 μm, in the case in which the particles are used as an internal electrode of multilayer ceramic capacitors. Furthermore, it is desirable that the specific surface area of the metallic powder by BET be in a range from 1 to 20 m^2/g. Furthermore, it is desirable that the particle shape of the metallic powder be spherical to improve sintering characteristics and dispersibility.

[0015] The present invention is based on a method in which raw metal and chlorine gas are reacted in a chlorination furnace to generate metal chloride vapor continuously, and the metal chloride vapor and hydrogen are reacted in a reduction furnace to obtain metallic powder continuously (hereinafter this may be called a "chlorination reduction method"). Generally, in a production method of metallic powder by such a vapor phase reduction reaction, a metal atom is generated at a moment when metal chloride vapor and hydrogen gas are contacted, the metal atoms collide and condense to generate ultrafine particles and the particles grow. The diameter of the generated metal powder is determined depending on conditions such as partial pressure of the metal chloride vapor or temperature. In this chlorination reduction method, the amount of the metal chloride vapor which is charged in the reduction furnace can be controlled by controlling the charged amount of chlorine gas since the metal chloride vapor is generated depending on the charged amount of the chlorine gas. In addition, since the metal chloride vapor is generated by a reaction of chlorine gas and metal, amount of carrier gas used can be reduced compared to a method in which metal chloride vapor is generated by heating and evaporating a solid of metal chloride. Furthermore, it is possible not to use carrier gas depending on production conditions. Therefore, production cost can be reduced by reducing the amount of carrier gas used and heating energy therefor.

[0016] In addition, the partial pressure of the metal chloride vapor in the reduction furnace can be controlled by mixing inert gas with the metal chloride vapor which is generated in the chlorination reaction. In this way, by controlling the charged amount of the chlorine gas or the partial pressure of the metal chloride vapor charged in the reduction furnace, the particle diameter of the metallic powder can be controlled, and not only can the diameter of metallic powder be stabilized, but also the diameter can be freely set.

[0017] As explained up to this point, the chlorination reduction method is superior from the viewpoints that metallic powder having consistent particle diameter can be obtained and that the metallic powder can be produced efficiently and at low cost. However, in the case in which the metallic powder is produced continuously by the chlorination reduction method, the chlorination reaction rate may be changed. If the chlorination reaction rate is changed, the amount of the metal chloride vapor which is generated in the chlorination furnace is changed and therefore the partial pressure of the metal chloride in the reduction furnace is changed, and as a result, particle sizes of the metal chloride vapor become nonuniform. There is a case in which metallic powder having desired particle diameter cannot be obtained. In particular in a production process for nickel powder for internal electrodes of a multilayer ceramic capacitor, coarse particles having diameters of not less than 1 μm or 2 μm may be greatly generated if such changing in chlorination reaction rate occurs.

[0018] For example, in a production process of nickel powder, raw nickel in a pelleted state of several millimeters is filled in the chlorination furnace, heated up to about 800°C, and chlorine gas and raw nickel are continuously charged to perform the chlorination reaction. At this time, raw nickel is chlorinated to generate nickel chloride vapor, and filled layer of raw nickel in the chlorination furnace is decreased. In this decreasing process, the chlorination reaction rate can be maintained constant if the filled layer of raw nickel is constantly decreased along the cross section of the chlorination furnace.

[0019] However, temperature distribution of the filled layer of raw nickel in the chlorination furnace is not uniform, and the central part or outer circumferential part of the filled layer of raw nickel may be selectively chlorinated and decreased depending on the position of chlorine gas charged in the chlorination furnace and the position of raw nickel. If such a non-uniform decreasing of filled layer of raw nickel is continued, gaps which penetrate the filled layer occur, and a part of the charged chlorine gas may be directly charged to the reduction furnace together with nickel chloride vapor without contacting raw nickel. If chlorine gas which is not reacted yet is charged directly in the reduction furnace, the partial pressure of the nickel chloride vapor in the reduction furnace is decreased and generating rate of nickel powder is increased owing to the existence of chlorine gas, and as a result, coarse particles are extremely increased.

[0020] The inventors have found that occurrence of the coarse particles is mainly caused by an inflow of chlorine gas which is not reacted yet in such chlorination reaction into the reduction furnace. Originally, such an abnormal phenomenon can be detected by determining composition of vapor and gas generated in the chlorination furnace continuously. However, a mixture gas of chlorine gas and metal chloride gas as in the present invention makes it difficult to perform separation and detection.

[0021] Therefore, it is desirable that changing rate of chlorination furnace weight be observed to perform feedback control of the chlorination reaction rate, since the chlorination reaction rate corresponds to the changing rate of chlorination furnace. As a controlling method of chlorination reaction rate, the amount of chlorine gas charged in the chlorination furnace can be reduced or the charged amount of the metal chloride vapor generated in the chlorination furnace to the reduction furnace can be reduced since deterioration of reaction rate mainly resulted from outflow of non-reacted chlorine gas through a penetrated gap which occurred in the filled layer of the raw metal in the chlorination furnace as described above. However, in these methods, overall productivity of metallic powder is deteriorated, reaction in the reduction furnace becomes uneven, and particle size of generated metallic powder may become nonuniform. Therefore, it is desirable that raw metal be charged in the chlorination furnace so as not to form gaps among filled layers of raw metal in the chlorination furnace. Usually, in a continuous operation, although raw metal is charged continuously or intermittently in the chlorination furnace, also in this case, it is desirable that the charged amount of the raw material be increased corresponding with detected decrease of reaction rate.

[0022] In addition, if the chlorine gas which is not contacted with raw metal and not reacted yet flows into the reduction furnace, the reaction rate of chlorination is radically decreased, particle size of generated metallic powder may be nonuniform if the phenomenon is allowed to remain as it is, and large amounts of coarse particles may be generated.

[0023] Therefore, in the present invention, it is desirable that the changing rate of the chlorination furnace weight be monitored and that the charged amount of the raw material be temporarily increased if an indication that the changing rate is deteriorated is observed. For example as shown in Fig. 4, if a fall in changing rate P is detected, the same or greater amount as an amount of the raw metal which is charged intermittently or continuously over 30 minutes is charged once or several times. After that, standard or lower amounts are charged intermittently or continuously. In this way, the condition of excess chlorine gas can be solved simultaneously. Therefore, the particle size of obtained metallic powder can be stabilized by decreasing the non-reacted chlorine gas which is charged in the reduction furnace, and in particular, generation of coarse particles can be reduced.

[0024] Specifically, it is desirable to use a load cell as a weighing method of chlorination furnace weight, and it is more desirable to use one which can detect the weight changing over time. In the present invention, changing in chlorination furnace weight is detected, weight changing amount per unit time is calculated, and this is controlled as the reaction rate. That is, this reaction rate means weight of metal chloride vapor generated per unit time. If this reaction rate is always maintained constant, the chlorination reaction is stabilized. Therefore, as a result, reaction in the reduction furnace is also stabilized and particle size of metallic powder obtained is also stabilized.

[0025] Furthermore, in the case in which the raw metal is charged in the chlorination furnace continuously or intermittently as described above, a raw material hopper in which raw metal is stored and charged is also weighed by the load cell. In this way, the reaction rate of chlorination can be detected and controlled by observing changing in weight of the raw material hopper and the chlorination furnace.

[0026] Desirable conditions of the method for production in the present invention are shown as follows.

> (1) A raw metal such as nickel metal is charged from a raw material hopper using a weighing method by a load cell, to a chlorination furnace using weighing method by a load cell, to form filled layer of the raw metal having a height to some extent.
> (2) After that, the chlorination furnace is heated and chlorine gas is charged in the chlorination furnace to start chlorination reaction.
> (3) At the same time, the raw metal is charged continuously or intermittently.
> (4) Reaction rate of chlorination reaction is continuously detected by a weight changing of the raw material hopper and the chlorination furnace.
> (5) Charging of the raw metal is increased to make the reaction rate reach a specific rate if changes, in particular decrease, of reaction rate is observed.

[0027] In the features described above, the production system of metallic powder in which the weights of raw material hopper and chlorination furnace are weighed, changes in chlorination reaction rate are detected, charged amount of raw metal is automatically controlled according to this, and reaction rate is controlled, is more desirable.

[0028] In the device of the present invention, as described above, since the chlorination furnace is arranged upstream of the reduction furnace, and since the both furnaces are connected directly, chlorination and reduction can be performed at the same time and continuously to produce metallic powder efficiently. Furthermore, since the metal chloride vapor is generated depending on the amount of the chlorine gas charged in the chlorination furnace and since the chlorination furnace and the reduction furnace are connected directly, the amount of the metal chloride vapor charged in the reduction furnace can be controlled by controlling the charged amount of the chlorine gas.

[0029] Furthermore, by arranging an inert gas charging pipe in the chlorination furnace, inert gas can be charged in the chlorination furnace to control the partial pressure of the metal chloride vapor in the reduction furnace. Therefore, the particle diameter of the metallic powder can be controlled by controlling the charged amount of the chlorine gas or the partial pressure of the metal chloride vapor which is charged in the reduction furnace. Furthermore, since a weighing method which can weigh the entirety of the chlorination furnace is prepared, changing of reaction rate in the chlorination reaction can be detected. By controlling this, it has become possible to stabilize the particle size of metallic powder and in particular to reduce generation of coarse particles. Furthermore, since a weighing method is also used in the raw material hopper, it becomes possible to control the reaction rate with greater accuracy.

[0030] Next, the production device for metallic powder of an embodiment of the present invention is explained further by way of drawings. It is desirable that chlorination reaction be performed in a chlorination furnace 5 shown in Fig. 1. The chlorination furnace 5 is supported by a load cell 9. A raw material hopper 1 which stores and charges raw metal 3 is arranged on the upper part of the chlorination furnace 5, and the raw material hopper 1 is connected to the top part of the chlorination furnace 5 by a raw metal charging pipe 21 in which raw metal charging valves 4a and 4b are arranged on the medium part thereof. The raw material hopper 1 is supported by a load cell 2, and the load cell 2 is connected to the load cell 9 of the chlorination furnace 5.

[0031] A chlorine gas charging pipe 6 is connected on the upper side part of the chlorination furnace 5, and an inert gas charging pipe 8 is connected on the lower side part. A heater 7 is arranged around the chlorination furnace 5, and a metal chloride vapor carrying pipe 12 is connected to the lower side part of the chlorination furnace 5. Both perpendicular type and horizontal type can be applied as the chlorination furnace 5, it is desirable to use perpendicular type so as to perform a solid-gas contact reaction uniformly. Furthermore, structures of medium parts of the raw material charging pipe 21, the chlorine gas charging pipe 6, and the inert gas charging pipe 8 have elasticity and flexibility such as bellows, and the weights of raw material hopper 1 and the chlorination furnace 5 can be weighed accurately. It should be noted that at the bottom part of the chlorination furnace 5, filler 11 is arranged to form a hearth. The filler 11 is composed of small pieces of, for example, quartz glass, and metal chloride vapor and inert gas can pass through the filler 11 while preventing falling of the raw metal.

[0032] Chlorine gas is caused to flow continuously through the chlorine gas charging pipe 6 and the flow amount thereof is measured. It is desirable that the chlorination furnace 5 and other members be composed of quartz glass. The metal chloride vapor carrying pipe 12 is connected to a metal chloride vapor injection nozzle 14 arranged on an upper end part of a reduction furnace 13, which is explained below.

[0033] Although the shape of the raw metal 3 which is a starting raw material is not limited in particular, from the viewpoints of contacting efficiency and prevention of pressure loss increasing, granular structures having diameters in a range of from 5 to 20 mm, massive structures, or plate structure is desirable. It is desirable that the purity be about 99.5% or more. Height of a filled layer of the raw metal 10 in the chlorination furnace 5 can be appropriately set in a sufficient range in which charged chlorine gas is converted to metal chloride vapor by considering such as chlorine charging rate, temperature of the chlorination furnace, continuous operation time, and shapes of the raw metal 3. The temperature in the chlorination furnace 5 can be set in a range in which the raw metal can be chlorinated, in the case of nickel metal, it is desirable in a range of from not less than 800°C which is necessary for proceeding the reaction, to not more than 1483°C which is a melting point of nickel. Considering the reaction rate and durability of the chlorinated furnace 5, it is desirable that it be in a range of from 900 to 1100°C in practice.

[0034] Chlorine gas is continuously charged from the chlorine gas charging pipe 6 to the chlorination furnace 5, and at the same time, the raw metal 3 is continuously or intermittently charged from the raw material hopper 1 by opening and closing the raw material charging valve 4. At this time, the charged amount of the raw metal is weighed by the load cell 2.

[0035] Metal chloride vapor generated in the chlorination furnace 5 can be carried to the reduction furnace 13 through the metal chloride vapor carrying pipe 12, or according to circumstances, 1 to 30 mol% to the metal chloride vapor of inert gas such as nitrogen or argon is mixed through the inert gas charging pipe 8, and this mixture gas is carried to the reduction furnace. This charging of inert gas can be a factor in controlling the particle diameter of the metallic powder. If too much inert gas is mixed, not only is too much of the inert gas consumed, but this also causes energy loss and is uneconomical. From these viewpoints, desirable partial pressure of the metal chloride vapor in the mixture gas which flows through the carrying pipe 12 is in a range of from 0.5 to 1.0 in the case in which total pressure is defined as 1.0. In particular, it is desirable that the partial pressure be in a range of from about 0.6 to 0.9 to produce fine metallic powders having diameters in a range from 0.15 to 0.5 μm. Furthermore, as described above, the generated amount of metal chloride vapor can be freely controlled by the charged amount of chlorine gas, and the partial pressure of the metal chloride vapor can be freely controlled by the charged amount of inert gas.

[0036] The metal chloride vapor which is generated in the chlorination furnace 5 is continuously carried to the reduction furnace 13. On the upper end part of the reduction furnace 13, metal chloride vapor injection nozzle 14 (hereinafter simply referred to as nozzle 14) which is connected to the metal chloride vapor carrying pipe 12 is projecting downward. Furthermore, on the upper end surface of the reduction furnace 13, hydrogen gas charging pipe 15 is connected, and cooling gas charging pipe 17 is connected on the lower side part of the reduction furnace 13. Furthermore, heater 16 is arranged around the reduction furnace 13. As is described below, the nozzle 14 has a function in which the metal chloride vapor (inert gas can be contained) is injected from the chlorination furnace 5 to the reduction furnace 13 in a desirable flowing rate.

[0037] In the process in which reduction of the metal chloride vapor by hydrogen gas is proceeding, reaction flame 18 which is like a burning flame of gas fuel such as LPG is formed extending downward from the top part of the nozzle 14. Charged amount of hydrogen gas to the reduction furnace 13 is chemical equivalent of the metal chloride vapor, that is to say, from 1.0 to 3.0 times chemical equivalent of chlorine gas which is charged to the chlorination furnace 5, desirably from about 1.1 to 2.5 times. But the charged amount of hydrogen gas is not particularly limited to these ranges. However, enormous hydrogen flow occurs in the reduction furnace 13 if too much hydrogen gas is charged. This hydrogen flow disturbs metal chloride vapor injecting flow which is injected from the nozzle 14, resulting in an uneven reduction reaction. In addition, it is uneconomical because gas which is not consumed may be emitted. Furthermore, although the required temperature of the reduction reaction is higher than a temperature which is sufficient to complete the reaction, a temperature less than a melting point of nickel may be used in the case of production of nickel powder because nickel powder in a solid state is easier to handle. Considering reaction rate, durability of the reduction furnace 13, and economic efficiency, temperature in a range of from 900 to 1100°C is practical. However, the temperature is not limited to this.

[0038] As described above, chlorine gas which is introduced into chlorination furnace 5 is converted to metal chloride vapor of the same mole amount, which is reduction raw material. The metallic powder 19 having appropriate particle diameter can be obtained by controlling liner velocity of flow of metal chloride vapor or a mixture of metal chloride vapor and inert gas, which is injected from the top of the nozzle 14. That is to say, if the diameter of the nozzle is constant, particle diameter of generated metallic powder 19 in the reduction furnace 13 can be controlled in a desired range by the charged amount of chlorine gas and inert gas sent to the chlorination furnace 5. Desirable linear velocity of gas flow (sum (calculated value which is converted to the charged amount of gas at the reduction temperature) of metal chloride vapor and inert gas) at the top of the nozzle 14 is set in a range from about 1 to 30 m/sec at a reduction temperature of from 900 to 1100°C, set in a range from about 5 to 25 m/sec in the case in which nickel powder of small particles having diameters of, for example, from 0.1 to 0.3 μm, is produced, and is set in a range of 1 to 15 m/sec in the case in which nickel powders having diameters from 0.4 to 1.0 μm are produced. The linear velocity in the axial direction of hydrogen gas in the reduction furnace 13 is desirably in a range from about 1/50 to 1/300 of the injection velocity (linear velocity) of the metal chloride vapor, and is more desirably in a range from 1/80 to 1/250. Therefore, substantially, the metal chloride vapor is injected from the nozzle 14 into a static hydrogen atmosphere. It is desirable that the exit of hydrogen charging pipe 15 be not directed toward the flame side.

[0039] In the method for production of the present invention, the particle diameter of metallic powder 19 generated in the reduction furnace 13 is decreased as the charged flowing amount of chlorine gas to the chlorination furnace 5 is increased, and conversely, the particle diameter is increased as the charged flowing amount of chlorine gas is decreased. Furthermore, by mixing inert gas with the metal chloride vapor near the exit of the chlorination furnace 5 to control the partial pressure of the metal chloride vapor, specifically by mixing inert gas for 1 to 30 mol% of the metal chloride vapor, for example, the particle diameter of the metallic powder can be increased by increasing the partial pressure, and conversely, the particle diameter of the metallic powder can be decreased by decreasing the partial pressure of the metal chloride vapor.

[0040] During the process in which the chlorination reaction is performed continuously in the chlorination furnace 5 and generated metal chloride vapor is reduced in the reduction furnace 13 to produce metallic powder as described above, weight change is detected continuously by weighing the weight of the chlorination furnace 5 by the load cell 9. On the other hand, the weight change of the raw material hopper 1 is continuously weighed by the load cell 2 to detect the weight of the raw metal 3 which is charged to the chlorination furnace 5. The reaction rate of the chlorination reaction is detected by these weight changes over time. That is to say, the sum of the weight change of the raw material hopper 1 per unit time and the weight change of the chlorination furnace 5 per unit time correspond to the weight of the metal chloride vapor which is generated in the chlorination furnace 5 per unit time, and further corresponds to the reaction rate (weight of generated metal chloride vapor/time) of the chlorination reaction.

[0041] This reaction rate is continuously observed through the production process of the metallic powder, and in the case in which an indication in which the reaction rate is deteriorated is observed, charging of the raw metal 3 from the raw material hopper 1 is immediately and temporarily increased to stabilize the reaction rate. Since the upper surface of the filled layer of raw metal 10 is uneven at this time, it is desirable that the raw metal be charged while observing visually, to make this upper surface even. Furthermore, it is desirable that the raw metal charging valve 4 and the weight change which is detected by the load cell 2 and 9 be interrelated by using, for example, a distributed controlling system, in the case in which indication of deterioration of reaction rate is observed, the metal charging valve 4 is opened and the raw metal 3 is charged so as to stabilize the reaction rate.

[0042] Cooling process can be arranged in the process for production of the metallic powder of the present invention. As shown in Fig. 1, the cooling process can be arranged in a space at the opposite side of the nozzle 14 in the reduction furnace 13, and alternatively, another casing which is connected to the exit of the reduction furnace 13 can be used. It should be noted that the cooling of the present invention means an operation which is performed to stop or to reduce growth of the metallic powder in gas flow (hydrochloric acid is included) generated at the reduction process, specifically an operation in which gas flow having temperature of about 1000°C after finishing the reduction reaction is quickly cooled to about 400 to 800°C. The cooling process can be performed to a lower temperature than this range.

[0043] As a desirable example of performing cooling, inert gas can be blown to a space downward of the top of the flame. Specifically, gas flow can be cooled by blowing nitrogen gas from cooling gas charging pipe 17. By blowing inert gas; the particle diameter of the metallic powder 19 can be controlled while clumping of the metallic powder is prevented. Cooling conditions can be freely changed by arranging the cooling gas charging pipe(s) at a point or plural points in the reduction furnace 13 along vertical direction. In this way, controlling of the particle diameter can be performed even more accurately.

[0044] The metallic powder 19 and the mixture gas of hydrochloric acid gas and inert gas which have passed through the processes described above are carried to a recovering process, and the metallic powder is separated and recovered from the mixture gas. Although it is desirable that combination of one kind or more selected from a bag filter, capture separation method in water, capture separation method in oil, and magnetic separation method be used to separate and recover the metallic powder, the methods of the present invention are not particularly limited. For example, in the case in which the metallic powder 19 is recovered by a bag filter, after the metallic powder 19 and the mixture gas of hydrochloric acid gas and inert gas which are generated in the cooling process are induced to the bag filter to recover only metallic powder 19, the metallic powder 19 can be carried to a washing process. In the case of the capture separation method in oil, normal paraffin having a carbon number of 10 to 18, or light oil, can be preferably used. In the case of the capture separation method in water or oil, clumping or oxidation of metallic powder particles can be effectively prevented by adding one or more kinds selected from polyoxyalkyleneglycol, polyoxypropyreneglycol or derivatives thereof (monoalkyl ether, mono ester), or surface active agent such as sorbitane, sorbitane monoester, known antioxidants such as phenol-based or amine-based metal deactivators represented by benzotriazole or derivatives thereof in a range from about 10 to 1000 ppm to a scavenger.

[0045] As explained above, in the method and device for production of the metallic powder by a conventional chlorination reduction method, uneven reaction occurring in the filled layer of the raw metal in the chlorination furnace causes flowing of non-reacted chlorine gas to the reduction furnace. Therefore, particle size of generated metallic powder is not stabilized, and in particular, coarse particles are generated. However, in the method and device of the present invention, reaction rate of the chlorination reaction can be controlled and stabilized by weighing the weight of the chlorination furnace, flowing of non-reacted chlorine gas to the reduction furnace can be prevented, and as result, the metallic powder having stable particle size and having no coarse particles can be produced. Furthermore, although reaction rate cannot be increased in the conventional method and device since the chlorination reaction is unstable being severely deteriorated as described above, the reaction rate can be increased in the present invention since the reaction rate is stabilized. As a result, productivity of the metallic powder can be improved.

Brief Description of the Drawings

[0046]

Fig. 1 is a longitudinal cross section showing a structure of the production device for metallic powder of the present invention.

Fig. 2 is a graph showing particle size distribution of nickel powder produced in Example and Comparative Example.

Fig. 3 (A) is a SEM photograph showing nickel powder produced in an Example, and (B) is a SEM photograph showing nickel powder produced in a Comparative Example.

Fig. 4 is a graph showing the reaction rate (changing rate of the chlorination furnace weight) in the chlorination furnace.

Explanation of Reference Numeral

[0047] 5...Chlorination furnace, 9...Load cell, 1...Raw material hopper, 2...Load cell, 13...Reduction furnace, 3...Raw metal

Best Mode for Carrying Out the Invention

[0048] The present invention is further explained in detail by way of an Example.

Example

[0049] 15 kg of raw nickel having average diameters of 5 mm was filled from raw material hopper 1 to a chlorination furnace 5 of a production device of metallic powder shown in Fig. 1, the temperature of the atmosphere in the furnace was maintained at 1100°C, and chlorine gas was induced by flow amount of 4 Nl/min to start chlorination reaction. After that, 0.5 kg of raw nickel was charged from the raw material hopper 1 to the chlorination furnace 5 intermittently every 5 minutes. Nickel metal was chlorinated in this way to generate nickel chloride vapor.

[0050] 10 mol% of charged amount of chlorine gas of nitrogen gas was mixed with this, and a gas mixture of nickel chloride vapor and nitrogen was induced from a nozzle 14 into a reduction furnace 13 in which the atmosphere was heated to 1000°C at a flow velocity of 2.3 m/sec (converted to in the case of 1000°C). At the same time, hydrogen gas was charged from the top part of the reduction furnace 13 at a flow velocity of 7 Nl/min to reduce nickel chloride vapor.

[0051] The chlorination reaction and the reduction reaction were concurrently and continuously conducted (for 30 hours), each weight of raw material hopper 1 and chlorination furnace 5 were weighed by a load cell 2 and 9, and the reaction rate of chlorination reaction in the chlorination furnace was continuously detected by the weight changing. Since an indication of deterioration in the reaction rate was observed 25 hours after starting of the production, charging amount of raw nickel was increased to 5 kg at one time to stabilize and the reaction rate, the production was continued.

[0052] Nitrogen gas was mixed with generated gas which is generated in the reduction reaction including nickel powder so as to cool in the cooling process. Then, mixed gas including nitrogen gas, hydrochloric acid vapor and nickel powder was introduced into pure water, and the nickel powder was separated and recovered. The obtained nickel powder was washed with pure water and dried to obtain a nickel powder product. The particle size distribution of the obtained nickel powder is shown in Fig. 2 and the SEM photograph is shown in Fig. 3 (A). Average particle diameter using a BET method was 0.40 μm, and the average particle diameter in the case in which the nickel powder was suspended in organic solvent was 1.50 μm. 0% of coarse particles having diameters not less than 5 μm was contained. The average particle diameters in the case in which the nickel powder was suspended in organic solvent and the particle diameter distribution was measured by the following method using a laser diffraction particle size analyzer (trade name: Coulter LS230, produced by Coulter). Optimum amount of metallic powder was suspended in α-terpineol, ultrasonic waves were applied to disperse for 3 minutes, the sample was measured in 1.8 of sample refraction factor, and the particle size distribution of statistic of volume was measured.

Comparative Example

[0053] Nickel powder was produced by a method similar to that in Example 1, except that the raw material hopper 1 and chlorination furnace 5 were not weighed and that the reaction rate of chlorination reaction in the chlorination furnace was not controlled. Particle size distribution of the obtained nickel powder is shown in Fig. 2 and a SEM photograph is shown in Fig. 3 (B). Average particle diameter using the BET method was 0.45 µm and the average particle diameter in the case in which the nickel powder was suspended in organic solvent was 1.45 µm. 3.0% of coarse particles having diameters not less than 5 µm was contained.

[0054] With respect to the particle size distribution of nickel powder which was produced in the method of the embodiment of the present invention, extremely low amounts of coarse particles are contained compared to nickel powder which is produced in the Comparative Example as shown in Fig. 2. Furthermore, it is obvious that coarse particles having particle diameters not less than 1 µm are contained in extremely small amount in the nickel powder produced in the Example as shown in the SEM photograph of Fig. 3, although coarse particles having particle diameters not less than 1 µm are contained to some extent in the nickel powder produced in the Comparative Example.

[0055] As explained above, metallic powder such as nickel powder used in, for example, internal electrodes of multilayer ceramic capacitors in which fine particle diameter not more than 1 µm is required can be produced efficiently, and furthermore, metallic powder having uniform particle diameter and having no coarse particles can be produced by controlling the reaction rate of the chlorination reaction, in the method for production and production device for the metallic powder in the present invention.

Claims

1. A method for production of metallic powder, the method comprising:

charging raw metal into a chlorination furnace intermittently or continuously,
reacting the raw metal and chlorine gas in the chlorination furnace to generate metal chloride vapor continuously;
continuously reacting the metal chloride vapor and hydrogen gas in a reduction furnace to obtain metallic powder;
weighing the weight of the chlorination furnace in which a chlorination reaction is proceeding; and
controlling an amount of the raw metal charged into the chlorination furnace according to the weighing result.

2. The method for production of the metallic powder according to claim 1, wherein weight changing rate of the chlorination furnace is observed, and charged amount of the raw metal to the chlorination furnace is controlled depending on the changing rate.

3. The method for production of the metallic powder according to claim 2, wherein the charged amount of the raw metal is temporarily and suddenly increased in the case in which the changing rate suddenly decreases.

4. The method for production of the metallic powder according to claim 2, wherein the changing rate is measured, the charged amount of the raw metal into the chlorination furnace is automatically controlled according to the measurement, and chlorination reaction rate of the raw metal and the chlorine gas in the chlorination furnace is controlled.

5. The method for production of the metallic powder according to one of claims 1 to 4, wherein the weight of the chlorination furnace is weighed by a load cell.

6. The method for production of the metallic powder according to one of claims 1 to 5, wherein the entirety of a raw material hopper which charges the raw metal into the chlorination furnace is weighed.

7. The method for production of the metallic powder according to one of claims 1 to 6, wherein the metal is nickel.

8. The method for production of the metallic powder according to claim 7, wherein the metallic powder is nickel powder having an average particle diameter in a range from 0.01 to 1 µm.

9. The method for production of the metallic powder according to claim 8, wherein the metallic powder is for a conductive paste.

10. The method for production of the metallic powder according to claim 8, wherein the metallic powder is for a multilayer ceramic capacitor.

11. A production device for the metallic powder, comprising:

a raw material hopper to charge raw metal;
a chlorination furnace to chlorinate the raw metal charged from the raw material hopper; and
a reduction furnace to reduce metal chloride vapor generated in the chlorination furnace;

wherein the raw material hopper and the chlorination furnace are communicated with a raw material charging pipe which charges the raw metal via a carrying valve for controlling charged amount thereof;

the chlorination furnace and the reduction furnace are communicated with a carrying pipe which carries metal chloride vapor generated in the chlorination furnace to the reduction furnace;

the chlorination furnace is comprising a chlorine gas charging pipe to charge chlorine gas inside;

the reduction furnace is comprising a nozzle to inject the metal chloride vapor inside, a hydrogen gas charging pipe to charge hydrogen gas inside, and a cooling gas charging pipe to charge inert gas for cooling the reduced metallic powder inside;

the producing device of the metallic powder further comprises a weighing method to weigh the entire weight of the chlorination furnace and a controlling method to control charged amount of the raw metal to the chlorination furnace depending on the weighing result of the weighing method.

12. The production for device of metallic powder according to claim 11, wherein the controlling method monitors the changing rate of the weight of chlorination furnace, and controls the charged amount of the raw metal into the chlorination furnace depending on the changing rate.

13. The production device for metallic powder according to claim 12, wherein the controlling method increases the charged amount of the raw metal temporarily and immediately in the case in which the changing rate is suddenly decreased.

14. The producing device for metallic powder according to claim 13, wherein the controlling method measures the changing rate, controls the charged amount of the raw metal into the chlorination furnace automatically according to the measurement, and controls the chlorination reaction rate of the raw metal and the chlorine gas in the chlorination furnace.

15. The production device for metallic powder according to one of claims 11 to 14, wherein the device further comprises a weighing means for weighing the weight of the entirety of the raw material hopper.

16. The production device for metallic powder according to one of claims 11 to 15, wherein the weighing means is a load cell.

17. The production device for metallic powder according to one of claims 11 to 16, wherein the metal is nickel.

Fig. 1

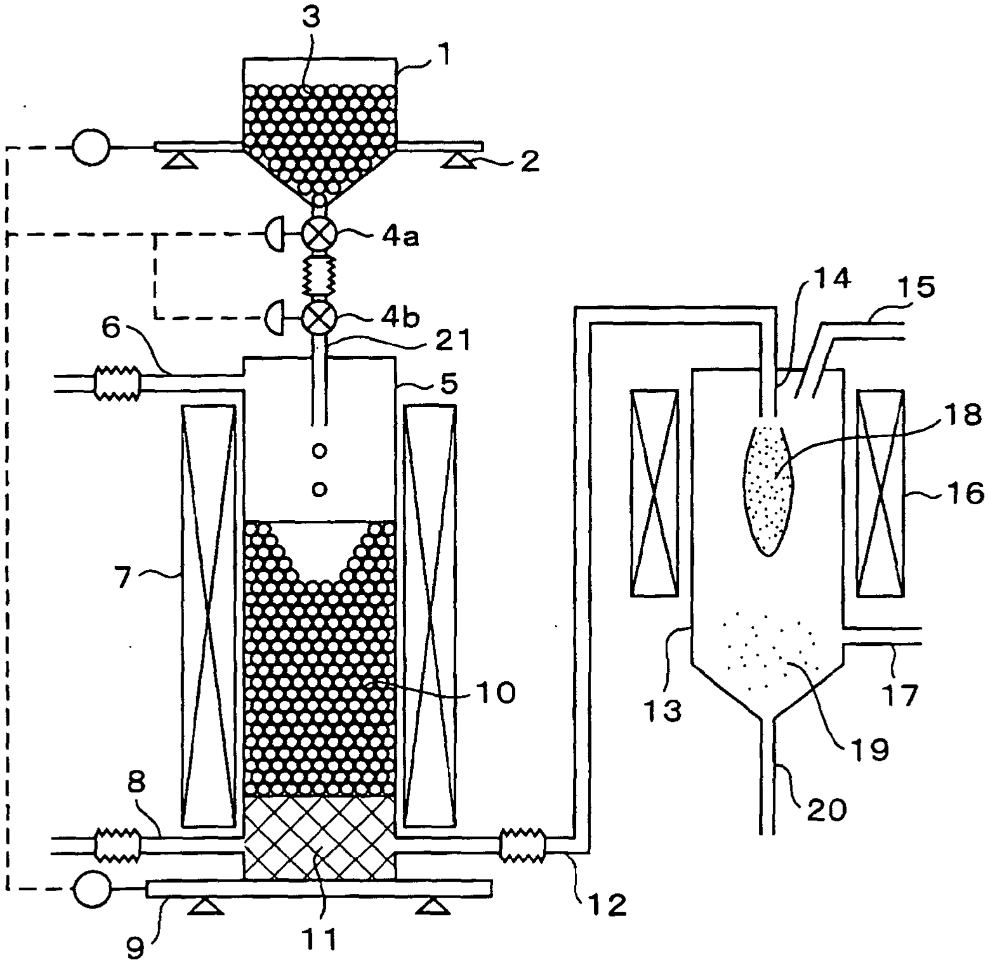


Fig. 2

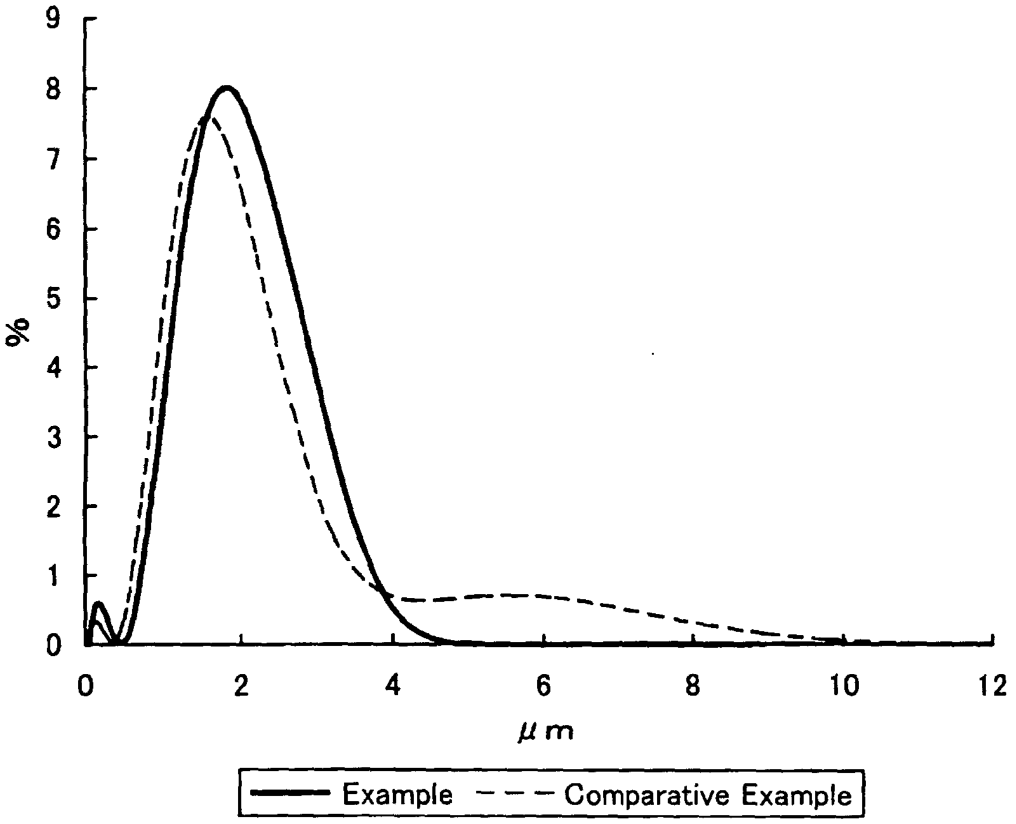


Fig. 3A

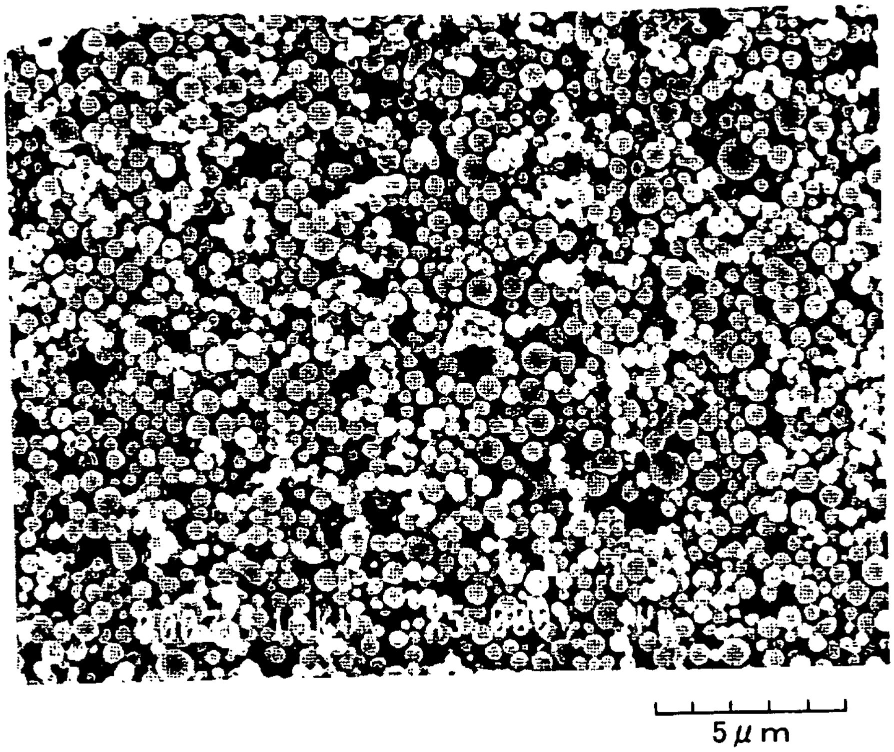


Fig. 3B

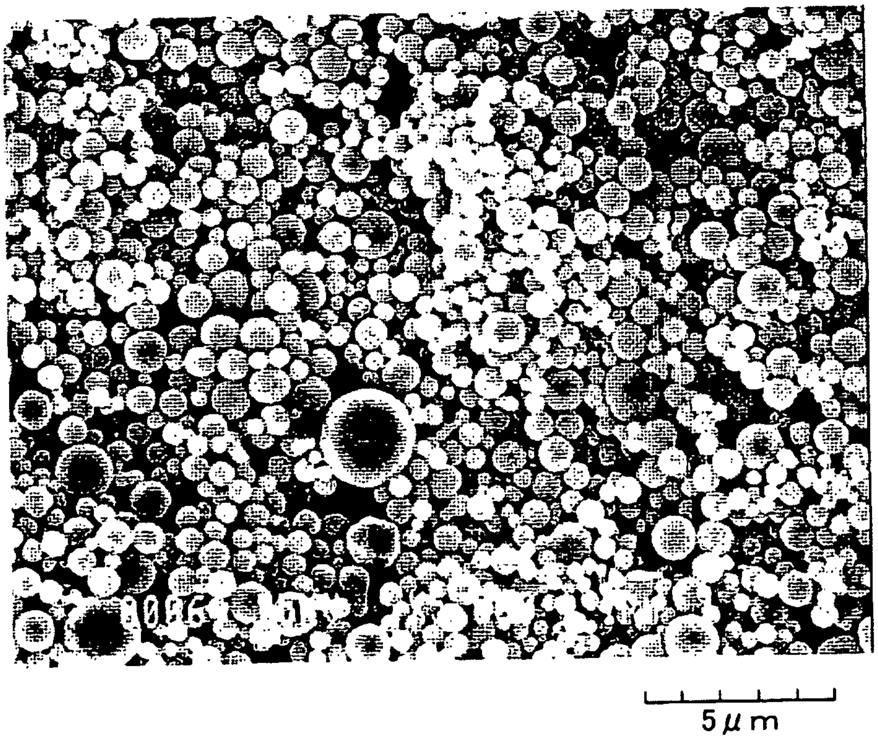
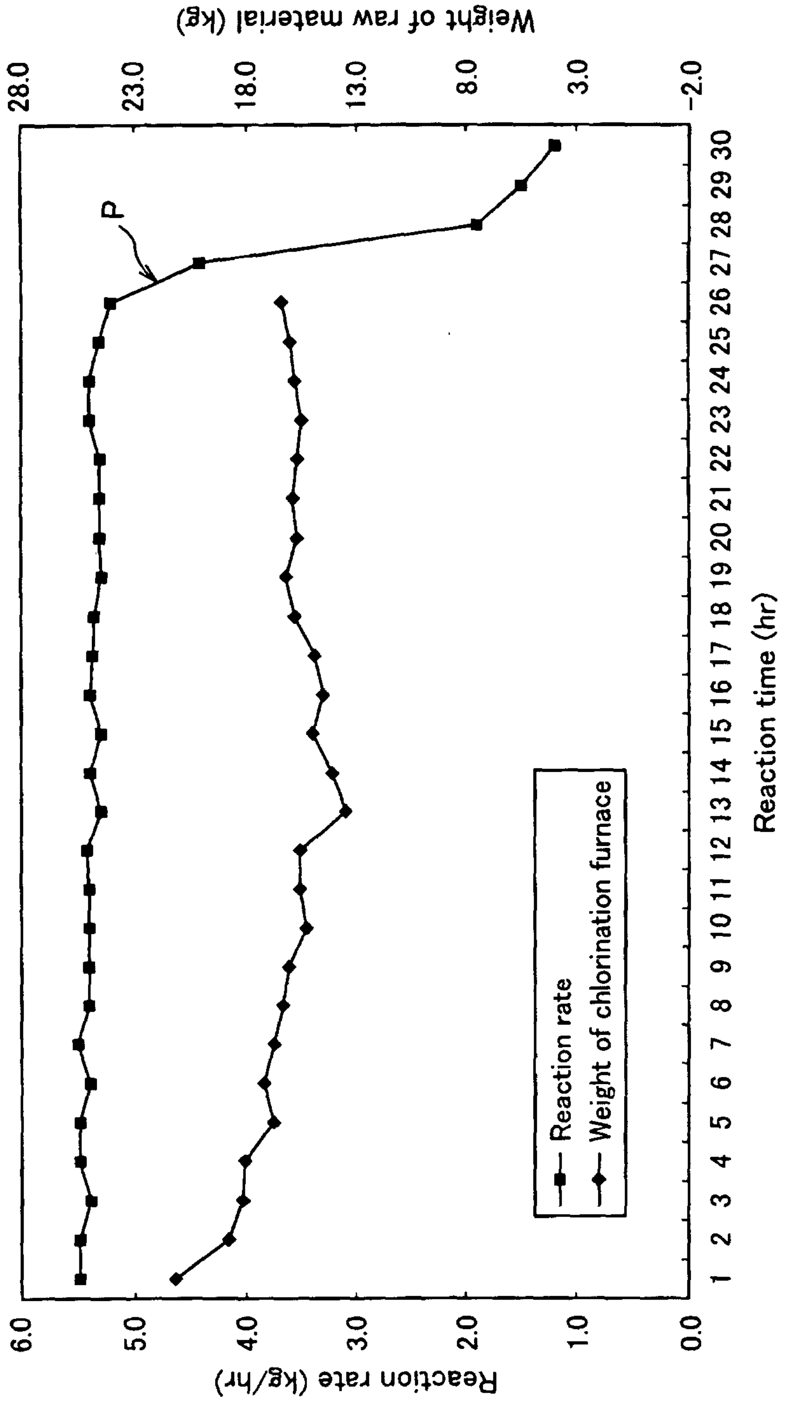


Fig. 4


Weight of raw material (kg)
28.0
23.0
18.0
13.0
8.0
3.0
−2.0
P
Reaction rate
Weight of chlorination furnace
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Reaction time (hr)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Reaction rate (kg/hr)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/06191

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 B22F9/28, H01G4/12, H01B1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 B22F9/18-9/28

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

Jitsuyo Shinan Koho	1922-1996	Toroku Jitsuyo Shinan Koho	1994-2003
Kokai Jitsuyo Shinan Koho	1971-2003	Jitsuyo Shinan Toroku Koho	1996-2003

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 2000-335905 A (TOHO TITANIUM CO., LTD.), 05 December, 2000 (05.12.00), Claims; Par. Nos. [0044], [0045] (Family: none)	1-17
A	EP 1114684 A1 (TOHO TITANIUM CO., LTD.), 11 July, 2001 (11.07.01), Claims; Par. No. [0009] & JP 2000-345219 A	1-17
A	EP 0887133 A1 (TOHO TITANIUM CO., TLD.), 30 December, 1998 (30.12.98), Claims; page 3, lines 1 to 3 & JP 10-219313 A	1-17

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

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"&" document member of the same patent family

Date of the actual completion of the international search 08 July, 2003 (08.07.03)	Date of mailing of the international search report 22 July, 2003 (22.07.03)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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