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(54) **TITANIUM POWDER AND METHOD FOR PRODUCING SAME**

(57) To provide titanium-based powder in which the pores in titanium powder are reduced. A titanium-based powder having a ratio of a pore area obtained by dividing a cross-sectional area of pores in a cross-section of the titanium-based powder by an area of the cross-section of the titanium-based powder is 0.3% or less. A method for producing a titanium-based powder includes a Hydro-

genation-DeHydrogenation method including a hydrogenation process, a pulverization process, and a dehydrogenation process using a titanium-based raw material is provided. A concentration of total MgCl_2 contained in the titanium-based raw material is 1.0 mass% or less, and a concentration of internal MgCl_2 contained in the titanium-based raw material is 0.1 mass% or less.

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Description

Technical Field

5 [0001] The present invention relates to a titanium-based powder, and more particularly, to an entirely novel titanium-based powder and a method for producing the same, which are produced by a Hydrogenation-DeHydrogenation method (hereinafter, referred to as an HDH method).

Background Art

10 [0002] Conventionally, little attention has been paid to pores in the titanium-based powder industrially, and there have been almost no literature or the like in which the pore generation mechanism is studied in detail. Recently, along with the demand for higher density of a sintered body using the titanium-based powder and the demand for higher quality to titanium products produced from the titanium-based powder, a demand for pore reduction in the titanium-based powder has been increasing.

15 [0003] Although the prior art document disclosing the technology which reduces the pore of the titanium based powder was investigated, it was not found. The prior art documents relating to the production of the titanium-based powder, include patent document 1 and patent document 2. In this specification, the titanium powder and titanium alloy powder are referred to as the titanium-based powder.

Prior art

Patent Literature

25 [0004]

Patent Literature 1: Japanese Patent Application Laid-Open No. H05-247503

Patent Literature 2: Japanese Patent Application Laid-Open No. H07-278601

Summary of Invention

Problem to be solved by the invention

35 [0005] The present invention is intended to solve the above problems, that is, to provide a titanium-based powder with reduced pores in the titanium-based powder.

Means for solving the problem

40 [0006] In order to achieve the production of the titanium-based powder having a small number of pores as described above, in the present invention, a structure and a mechanism of a generation of the pores were analyzed in detail. As a result, it was found that the number of pores generated was significantly changed by adjusting the raw material and the producing method of the titanium-based powder, and we focused on the analysis results that the generation of pores was the pores having a substantially circular (spherical) cross-sectional shape remain due to the presence of gas (or the presence of gas in the past) in the titanium-based powder.

45 [0007] According to an embodiment of the present invention, a titanium-based powder having a ratio of a pore area obtained by dividing a cross-sectional area of pores in a cross-section of the titanium-based powder by an area of the cross-section of the titanium-based powder is 0.3% or less is provided.

[0008] The titanium-based powder may be HDH powder.

50 [0009] According to an embodiment of the present invention, a method for producing a titanium-based powder includes a Hydrogenation-DeHydrogenation method including a hydrogenation process, a pulverization process, and a dehydrogenation process using a titanium-based raw material is provided. A concentration of total $MgCl_2$ contained in the titanium-based raw material is 1.0 mass% or less, and a concentration of internal $MgCl_2$ contained in the titanium-based raw material is 0.1 mass% or less.

[0010] The titanium-based raw material may have a maximum thickness of 20 mm or less.

55 [0011] A hydrogenation titanium-based powder may be pulverized to have a D95 particle size of 300 μm or less in the pulverizing process.

[0012] The titanium-based raw material may be hydrogenated within a temperature range of 716°C or more and 1050°C or less over a period of 90 minutes or more in the hydrogenation process.

Effects of Invention

[0013] The pore generation in titanium-based powder is closely related to gas. The number of titanium-based powders containing pores can be significantly reduced by not entraining gas in the titanium-based powder, not generating gas inside the titanium-based powder, or by quickly removing the generated gas from inside the titanium-based powder.

Brief Description of Drawings

[0014]

Figure 1 is a diagram for showing a method of image processing, particularly showing an encapsulated pore;
 Figure 2 is a diagram for showing a method of image processing, showing an opened pore;
 Figure 3 is an optical micrograph of the titanium powder according to Example 1;
 Figure 4 is an optical micrograph of the titanium powder according to Example 3; and
 Figure 5 is a photograph when the image processing was performed in an optical micrograph of the titanium powder according to Comparative Example 2.

Description of Embodiments

[0015] Most of the titanium powder is currently made from sponge titanium produced by the Kroll method. In some cases, scrap is used as a raw material from the viewpoint of economic efficiency and resource protection.

[Description of the Kroll method].

[0016] The Kroll method is a method of obtaining metallic titanium by reducing titanium tetrachloride (TiCl_4) obtained by chlorinating titanium ore with magnesium (Mg).

[0017] In the Kroll method, since MgCl_2 generated in the reduction process ($\text{TiCl}_4 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgCl}_2$) coexists with the sponge titanium, the sponge titanium after MgCl_2 is removed in the separation process is used. However, when the sponge titanium was examined thoroughly, it was found that MgCl_2 was not completely removed, and 2 types of MgCl_2 remained: MgCl_2 attached to the surface of the sponge titanium (surface MgCl_2) and MgCl_2 trapped inside the sponge titanium and isolated from the outside (inner MgCl_2).

[0018] MgCl_2 remaining on the surface of the sponge titanium (surface MgCl_2) which is not sufficiently removed in the separation process can be removed by applying heat in a reduced pressure again. On the other hand, when the inside was examined by cutting the sponge titanium after applying heat under reduced pressure, it was found that MgCl_2 trapped inside the sponge titanium (inner MgCl_2) cannot be removed by this method.

[Description of the method for producing the titanium powder by the atomization method]

[0019] The method for producing the titanium powder is roughly divided into the atomization method and the HDH method. In the atomization method, the titanium powder is produced by melting titanium raw material, forming fine liquid particles of titanium liquefied in the Ar gas, and simultaneously quenching and solidifying the particles.

[0020] In our research investigation of the present invention, it was concluded that there are two mechanisms in which the pores are generated in the titanium powder in the atomization method. The first is a mechanism in which MgCl_2 present inside the titanium raw material (inner MgCl_2) is gasified at once and rapidly quenched, whereby the gasified MgCl_2 is trapped inside the particles of the liquefied titanium so that the pores are generated in the titanium powder. The second is a mechanism in which the liquefied titanium particles are solidifying by incorporating Ar gas or vaporized MgCl_2 gas so that the pores are generated in the titanium powder. Therefore, it has been concluded that the HDH method is suitable for achieving the object of the present invention.

[Description of the method for producing the titanium powder by the HDH method]

[0021] The HDH method is a method of obtaining the titanium powder by once hydrogenating titanium raw material to form fragile TiH_2 , then pulverizing and dehydrogenating. In other words, it is a method for producing the titanium powder (HDH powder) by a process of hydrogenation, pulverization, dehydrogenation, and crushing. The above crushing process is optional, but in the production of the titanium powder (HDH powder) is preferably subjected to a crushing process.

[0022] At this time, in the process of hydrogenation, the titanium raw material is charged into a vacuum replaceable hydrogenation furnace, hydrogenated at a temperature of 400°C or higher in hydrogen gas atmosphere, and obtained

the body of titanium hydride by substituting the Ar gas atmosphere from the hydrogen gas atmosphere. The titanium raw material is hydrogen embrittled by the process of hydrogenation.

[0023] The next step is the pulverization process. In the pulverization process, the body of titanium hydride is mechanically pulverized to the titanium hydride powder having a mechanical fractured surface, a pulverized surface. The resulting titanium hydride powder is classified and/or sieved to remove the fine powder of titanium hydride. The pulverization device such as a ball mill or a vibration mill may be used for the mechanical pulverization of titanium hydride, and a sieve separation device such as a circular vibrating sieve or an air flow classifier may be used for adjusting the particle size of the titanium hydride powder.

[0024] In the dehydrogenation process, the above-mentioned titanium hydride powder is put into a container, charged into a dehydrogenation furnace of a vacuum heating type, and obtain the dehydrogenated titanium powder, for example, by heating at the temperature of 450°C or more in a vacuum of 10^{-3} Torr (0.13Pa) or less. Ar gas is inserted in the container as needed.

[0025] In the crushing process, unraveling the temporary sintered portion of the body of dehydrogenated titanium temporary sintered in the dehydrogenation process, and returning to the titanium powder shape having a pulverized surface or a crushed surface after pulverization.

[Description of the mechanism of the pore generation in the HDH method]

[0026] The present inventors have studied and investigated the conditions in each producing process of the HDH method in detail from the viewpoint of the pores, and examined how to prevent the generation of the pores. In the HDH method, if titanium is not melted and liquefied during each producing process, Ar gas in the atmosphere is not incorporated and does not cause the pores. Heat treatment in the HDH method is consisting of two processes of hydrogenation and dehydrogenation, both of them should be performed below the melting point. However, since stainless steel is generally used as a container for containing the titanium material, when the iron contained in the stainless steel and titanium came into contact with each other and the temperature of both becomes equal to or higher than the eutectic temperature of iron and titanium, titanium becomes a liquid and does not meet the above purpose. Therefore, the present inventor has found that it is necessary to control titanium below the eutectic temperature of iron and titanium and prevent the liquefaction of titanium in order to prevent the generation of the pores. That is, it becomes an important component of the present invention to control the upper limit of the temperature.

[0027] For example, in Patent Document 1 and Patent Document 2, there is only described that the temperature has been raised to 650°C in the vacuum atmosphere, and there is no description about the temperature control of the titanium material after the subsequent introduction of the hydrogen gas. Since the hydrogenation reaction for hydrogenating titanium is an exothermic reaction, initially, for example, hydrogen absorption is performed at 650°C in a vacuum furnace, but thereafter, the temperature rises spontaneously. Therefore, it is necessary to finely control how to put into the container of titanium material, the charge amount of hydrogen and Ar, the charging time, and cooling to suppress the temperature rise while constantly observing the temperature of each site etc., so that the eutectic temperature or less at any location including a local.

[0028] The boiling point of $MgCl_2$ at normal pressure is 1412°C, and at this temperature, $MgCl_2$ trapped inside the titanium raw material (inner $MgCl_2$) gasifies. On the other hand, since the melting point of titanium is 1668°C, titanium is present in the solid state at 1412°C. The gasified inner $MgCl_2$ has a larger volume compared to the solid state, which causes a very high pressure state to be formed inside the titanium. This high pressure condition due to the gasified inner $MgCl_2$ generates cracks in the hydrogenated titanium which has become embrittled by hydrogenation, from which $MgCl_2$ can be discharged to the outside of the titanium hydride.

[0029] However, as described above, in the HDH method, the container containing the titanium material is often stainless steel, and it cannot be raised above the eutectic temperature of iron and titanium (1085°C). In the present invention, it has been found that an unconventional control method which adheres to this limited temperature and removes $MgCl_2$ responsible for the pore has been found, and has completed the present invention. In other words, $MgCl_2$ is set to liquid phase by setting the temperature of the titanium raw material to a temperature equal to or higher than the melting point of $MgCl_2$ (714°C) at a minimum, and the volume of $MgCl_2$ is expanded relative to the state of the solid. At this time, since titanium is present in the solid state, the inner $MgCl_2$ has a larger volume in the liquid state than in the solid state, which causes a very high pressure state inside the titanium. This high pressure condition due to the inner $MgCl_2$ of liquid phase causes cracking in the hydrogenated titanium which has become embrittled by hydrogenation. $MgCl_2$ of liquid phase exposed to the outside of the titanium by cracking is allowed to vaporize by gradual evaporation. The control of the temperature and heating time (maintaining time of the temperature) in the furnace in this case is also determined by considering the thickness and hydrogenation time of the titanium raw material to be hydrogenated. This result in the formation of the spherical pores inside the titanium because, for example, if the pressure inside the titanium is increased by the evaporated $MgCl_2$ before the titanium is embrittled, the titanium at high temperature is easily deformed softened. This is the opposite of the present invention. For example, in the present invention, by applying a time of 90 minutes or

more in a range of 716°C or more and 1050°C or less, MgCl_2 present inside the titanium raw material evaporates from the cracks of titanium, it is also possible to realize the hydrogenation of titanium. Theoretically, the temperature of the titanium raw material can be set in a range from the melting point of MgCl_2 (714°C) or more to less than the eutectic temperature of iron and titanium (1085°C), but more reliable temperature control can be performed by setting the above temperature range.

[0030] In the HDH method according to the present embodiment, titanium of the raw material is prevented from being melted by controlling the temperature. However, since MgCl_2 is vaporized during the process of the HDH method if MgCl_2 is attached to the surface of the titanium raw material, it is preferable to make it high-vacuum in order to remove MgCl_2 of the surface. In the HDH method according to the present embodiment, it is important to reduce the amount of MgCl_2 attached to the surface brought together with the titanium raw material, and optimize the temperature, time, degree of vacuum, Ar-substitution and the like in consideration of the cost.

[0031] In the hydrogenation process according to the present embodiment, in order to prevent the generation of pores and to remove MgCl_2 present inside the titanium (inner MgCl_2), a hydrogenation process of embodying the above-described mechanism found in the present invention. Although it is possible to discharge MgCl_2 if embrittlement by hydrogenation is carried out in enough time, it is not industrially appropriate in terms of productivity and cost.

[0032] As a result of the investigation, it was proven that controlling the amount of MgCl_2 existing in the inside of the titanium raw material has a greater effect on the productivity and the cost than controlling the amount of MgCl_2 attached to the surface of the titanium raw material. Various experiments showed that the total MgCl_2 concentration of the titanium raw material should be kept at 1.0 mass% or less. Then, the total MgCl_2 concentration of the titanium raw material is preferably suppressed to 0.05 mass% or less, more preferably suppressed to 0.001 mass% or less. In particular, if MgCl_2 concentration present in the interior of the titanium raw material (inner MgCl_2 concentration) is 0.5 mass% or less, it was found that it is possible to efficiently remove MgCl_2 responsible for the pores even when the time of maintaining the temperature of the titanium raw material in the range from the melting point of MgCl_2 (714°C) or more to less than the eutectic temperature of iron and titanium (1085°C) is 90 minutes in the HDH method. The effect is more clearly exhibited by setting the MgCl_2 concentration present in the interior of the titanium raw material (internal MgCl_2 concentration) to 0.1 mass% or less. In the present invention, the MgCl_2 concentration trapped inside the titanium raw material (internal MgCl_2 concentration) is preferably 0.1 mass% or less, more preferably 0.001 mass% or less.

[Method for suppressing the pore in raw materials]

[0033] In the HDH method of the present invention, since titanium does not melt, there is no generation of the pores due to entrainment of Ar gas or the like.

[0034] As a method of suppressing the total MgCl_2 concentration of the titanium raw material to 1.0 mass% or less and further suppressing the MgCl_2 concentration trapped in the titanium raw material (inner MgCl_2 concentration) to 0.1 mass% or less, although costly, it is also effective to make the sponge titanium finer in advance and heat-treat it again in a vacuum.

[0035] The titanium raw material has a maximum thickness of 20mm or less, more preferably 10mm or less. By the maximum thickness of the titanium raw material is 20mm or less, hydrogen is sufficiently diffused inside the raw material during hydrogenation for rapidly causing cracks to embrittle titanium.

[Defining total MgCl_2 concentration]

[0036] The method of measuring the concentration of total MgCl_2 is described. The chlorine concentration of the target titanium raw material is measured by a silver nitrate titration method (JIS H 1615). The value of the chlorine concentration is converted into the MgCl_2 concentration, and this is defined as MgCl_2 concentration (total MgCl_2 concentration) contained in the titanium raw material.

[Defining Inner MgCl_2 concentration]

[0037] The method of measuring the concentration of the inner MgCl_2 is described. First, the target titanium raw material is heat-treated under reduced pressure (50pa or less) at about 750°C for 1 hour to remove MgCl_2 of the surface. Thereafter, the chlorine concentration of the present material is measured by a silver nitrate titration method (JIS H 1615). The value of the chlorine concentration is converted into the MgCl_2 concentration, and this is defined as an MgCl_2 concentration trapped and present inside the titanium raw material (internal MgCl_2 concentration).

[Description of the size of the titanium powder]

[0038] In the pulverizing process, by crushing the hydrogenated titanium hydride to fine titanium hydride powder having

a pulverized surface, it is possible to further increase the probability that the pores remaining in the titanium hydride will be cracked as the starting point and will be opened. The probability that the pores are opened will be higher if the particle diameter of the titanium hydride powder is finer. However, since there is an industrial cost and time limitation, the particle diameter of the titanium hydride powder may be 300 μm or less, preferably 150 μm or less. Here, the particle diameter of the titanium hydride powder produced and pulverized by the HDH method has a distribution, and 95% or more of the particle diameter of the total titanium hydride powder may be equal to or less than the above value. In other words, the D95 particle diameter of the titanium hydride powder is 300 μm or less, and it is more effective if the D95 particle diameter is suppressed to 150 μm or less. The lower limit of the D95 particle diameter is not particularly limited, but may be 70 μm or more, and may be 80 μm or more, as an example. In the present invention, D95 refers to a particle size at which a volume-based cumulative distribution is 95% in a particle size distribution measurement obtained by a laser diffraction/scattering method. For details, it is measured based on JIS Z8825:2013.

[0039] 95% or more of the total titanium particle diameter of the titanium powder produced and crushed by the HDH method may be 150 μm or less.

[Application to the spheronization process]

[0040] The titanium powder produced by the HDH method described above has less MgCl_2 residue. For this reason, the titanium powder produced by the HDH method of the present invention is suitable as a raw material powder for obtaining a spherical powder by melting (e.g., plasma melting) the surface of the titanium powder, and spheronizing the angular surface which is a pulverized surface or a crushed surface. Since the titanium powder produced and crushed by the HDH method has a pulverized surface or a crushed surface having an uneven structure, it is possible to promote melting when introduced into the plasma due to its wide surface area. Since there is no entrainment of plasma gas such as Ar even if the titanium powder surface is melted to spheronize, new pores can be suppressed.

[0041] As described above, in order to suppress the pore generation in the HDH method, it is necessary to appropriately controlling the temperature, time, amount of hydrogen blown, material shape, and amount of MgCl_2 brought in (the total amount and the internal amount of MgCl_2) as described above, and thus the present invention has been completed.

[0042] The present embodiment has been described based on the titanium powder. However, even in the titanium alloy powder containing an element such as 50 mass% or less of Al or V to titanium, the raw material titanium alloy is prevented from melting by controlling the temperature by the HDH method, and the same effect as the titanium powder can be obtained. The element to be contained in titanium is preferably 20 mass% or less, more preferably 15 mass% or less. The titanium alloy powder may contain multiple types of elements. For example, the titanium alloy powder may be Ti-Al-V alloy powder. In this case, the Ti-Al-V powder can have an Al content of 5.5 to 7.5 mass% and a V content of 3.5 to 4.5 mass%.

[Explanation of the pore area ratio of the cross-section]

[0043] By the method for producing the titanium-based powder according to the present embodiment, the value (pore area ratio of the cross section) obtained by dividing the cross-sectional area of the encapsulated pores (hereinafter referred to as internal pores) observed in any cross-section of the titanium-based powder by the area of the cross-section of the titanium-based powder can be realized 0.3% or less. It is preferable that the titanium-based powder produced in the present invention has a number of the inner pores which appear by observing an arbitrary cross-section of the titanium-based powder of 20pieces/ mm^2 or less per unit area. Here, the pore area ratio of the titanium-based powder cross-section of 0.3% or less means that, after embedding the titanium-based powder in the resin and polishing, a value obtained by dividing the cross-sectional area of the inner pore observed as an image ranging from the brightness of 90 to 250 by the total cross-sectional area of the powder is 0.3% or less by the image processing, when the cross-section is observed by an optical microscope at a magnification of 500 times and an arbitrary location of 700 μm ×500 μm size is observed at 16 locations. The number of the internal pores means the number of the internal pores observed as images in the range of brightness 90-250 by image processing during the above observation. In any observation, the powder having a major axis of 10 μm or less is excluded by image processing. In the image processing, the pores that are apparently open from the original image even though they appear to be the internal pores were excluded (FIG.1 is a photograph before image processing and FIG.2 is a photograph after image processing). Even if the two pores were clearly in contact, they were calculated as one as long as they were one internal pore connected by image processing. In the present invention, since the pore area ratio of the above cross-section is 0.3% or less, the titanium powder produced by the manufacturing method according to the present invention is suitable for use in a technical field in which the pores must be small(e.g., an Air-craft material or the like). On the other hand, it has been found that when the pore area ratio of the cross-section exceeds 0.3 percent, it is difficult to use in the technical field.

[Examples]

[Example 1]

- 5 **[0044]** The sponge titanium was used as the titanium raw material. The titanium raw material had total MgCl_2 concentration and internal MgCl_2 concentration of 0.05mass% or less, and a diameter of 1/2 inch or less.
- [0045]** After vacuuming 300kg of the raw material to 5Pa or less, the atmosphere was heated to 650°C with a heater, and held for 120 minutes. Thereafter, hydrogen was supplied to cause a reaction of hydrogen adsorption and heat generation, and the titanium raw material was hydrogenated for 120 minutes while controlling the temperature so as to be 1000°C or less by controlling the heater, insertion of Ar gas, and operating the cooling device. The temperature range at this time was 716°C or more and 1000°C or less.
- 10 **[0046]** The bulk density of the titanium raw material at the process of hydrogenation was 1.2g/cm³.
- [0047]** Subsequently, the body of titanium hydride was pulverized by a pulverizer/classifier to obtain the titanium hydride powder having a particle diameter of 10μm to 150μm.
- 15 **[0048]** After performing dehydrogenation treatment in a vacuum heat treatment furnace condition, the body of dehydrogenated titanium was subjected to crushing treatment. The D95 particle diameter of the obtained titanium powder was 100μm.
- [0049]** The optical micrograph of the obtained titanium powder is shown in FIG.3. Titanium powder was embedded in the resin, polished the cross-section of the sample, and observed at 16 locations of arbitrary locations of 700μm×500μm size with an optical microscope at a magnification of 500. As a result of analyzing, the number of pores and the area ratio, the number of detected pores was 20pieces/mm² per unit area. The pore area ratio was 0.11%.
- 20

[Example 2]

- 25 **[0050]** The chip produced using the sponge titanium raw material having a total MgCl_2 concentration of 0.1 mass% or less, having a total MgCl_2 concentration of 0.0002 mass% or less and a maximum thickness of 7mm thereof was used as a titanium raw material. That is, the inner MgCl_2 concentration of the titanium raw material was also 0.0002 mass% or less. After vacuuming 300kg of the raw material to 5Pa or less, the atmosphere was heated to 650°C with a heater, and held for 120 minutes. Thereafter, hydrogen was supplied to cause a reaction of hydrogen adsorption and heat generation, and the titanium raw material was hydrogenated for 120 minutes while controlling the temperature so as to be 1000°C or less by controlling the heater, insertion of Ar gas, and operating the cooling device. The temperature range at this time was 716°C or more and 1000°C or less.
- 30 **[0051]** The bulk density at the process of hydrogenation was 1.2g/cm³. Subsequently, the body of titanium hydride was pulverized by a pulverizer/classifier to obtain the titanium hydride powder having a particle diameter of 10μm to 150μm. After performing dehydrogenation treatment in a vacuum heat treatment furnace condition, the body of dehydrogenated titanium was subjected to crushing treatment. The D95 particle diameter of the obtained titanium powder was 100μm.
- 35 **[0052]** Titanium powder was embedded in the resin, polished the cross-section of the sample, and observed at 16 locations of arbitrary locations of 700μm×500μm size with an optical microscope at a magnification of 500. As a result of analyzing, the number of detected pores was 8pieces/mm² per unit area. The pore area ratio was 0.02%.
- 40 **[0053]** In the above Example 2, the titanium powder was produced from two types: the titanium raw material having the concentration of iron as an impurity of 200 ppm by mass or less and the titanium raw material having the concentration of iron of more than 200 ppm by mass and 500 ppm by mass or less. In all cases, the number of detected pores ranged from 8 to 10pieces/mm² per unit area. In all cases, the pore area ratio was 0.02%. Therefore, it is considered that the amount of iron as an impurity, in other words, the purity of titanium, is not correlated with the behavior of the pore.
- 45

[Example 3]

- 50 **[0054]** The 90%Ti-6%Al-4%V (mass%) chips produced using the sponge titanium raw material having a total MgCl_2 concentration of 0.1 mass% or less and an alloy of 60%Al-40%V was used as the raw material. The total MgCl_2 concentration of the titanium-alloy chips used as a raw material was 0.0002 mass% or less, and its maximum thickness was 7mm. That is, the inner MgCl_2 concentration of the titanium-alloy chips was also 0.0002 mass% or less. After vacuuming 300kg of the raw material to 5Pa or less, the atmosphere was heated to 650°C with a heater, and held for 120 minutes. Thereafter, hydrogen was supplied to cause a reaction of hydrogen adsorption and heat generation, and the titanium alloy chip was hydrogenated for 120 minutes while controlling the temperature so as to be 1000°C or less by controlling the heater, insertion of Ar gas, and operating the cooling device. The temperature range at this time was 716°C or higher 1000°C or less.
- 55 **[0055]** The bulk density at the process of hydrogenation was 1.2g/cm³. Subsequently, the body of titanium hydride

was pulverized by a pulverizer/classifier to obtain the powders of 10 μ m to 150 μ m. After performing dehydrogenation treatment in a vacuum heat treatment furnace condition, the body of dehydrogenated titanium was subjected to crushing treatment. The D95 particle diameter of the obtained titanium powder was 100 μ m.

[0056] Titanium alloy powder was embedded in the resin, polished the cross-section of the sample, and observed at 16 locations of arbitrary locations of 700 μ m $\times$ 500 μ m size with an optical microscope at magnification of 500. As a result of analyzing, the number of detected pores was 9pieces/mm² per unit area. The pore area ratio was 0.03%.

[0057] The titanium alloy powder obtained above was spheroidized by melting the surface by Ar gas as a plasma gas using the high-frequency heat induction plasma apparatus. The conditions for spheronization are as shown in Table 1. An optical micrograph of the obtained titanium alloy powder is shown in FIG.4. The titanium alloy powder was embedded in the resin, and the cross-section of the sample was observed at 16 locations of arbitrary locations of 700 μ m $\times$ 500 μ m size with an optical microscope at magnification of 500. As a result of analyzing the number of pores and area ratio, and the number of detected pores was 3pieces/mm² per unit area. The pore area ratio was 0.01%. The titanium alloy powder produced and crushed by the HDH method was confirmed to be useful as a raw material powder of the spherical powder.

[Table 1]

Feed speed (kg/hr)	Transmission frequency (MHz)	Coil power (kW)	Plasma gas (l/min)	
			Ar	H ₂
0.28	3.5	20	76	3

[Example 4]

[0058] The 89%Ti-7%Al-4%V (mass%) chips produced using the sponge titanium raw material having the total MgCl₂ concentration of 0.1 mass% or less and an alloy of 70%Al-40%V was used as the raw material. The total MgCl₂ concentration of the titanium-alloy chips used as the raw material was 0.0002 mass% or less, and its maximum thickness was 2mm. That is, the inner MgCl₂ concentration of the titanium-alloy chips was also 0.0002 mass% or less. After vacuuming 300kg of the raw material to 5Pa or less, the atmosphere was heated to 650°C with a heater, and held for 120 minutes. Thereafter, hydrogen was supplied to cause a reaction of hydrogen adsorption and heat generation, and the titanium alloy chip was hydrogenated for 120 minutes while controlling the temperature so as to be 1000°C or less by controlling the heater, insertion of Ar gas, and operating the cooling device. The temperature range at this time was 716°C or higher 1000°C or less.

[0059] The bulk density at the process of hydrogenation was 1.2g/cm³. Subsequently, the body of the titanium hydride was pulverized by a pulverizer/classifier to obtain the powder of 10 μ m to 150 μ m. After performing dehydrogenation treatment in a vacuum heat treatment furnace condition, the body of dehydrogenated titanium was subjected to crushing treatment. The D95 particle diameter of the obtained titanium powder was 100 μ m.

[0060] Titanium alloy powder was embedded in resin, polished the cross-section of the sample, and observed at 16 locations of arbitrary locations of 700 μ m $\times$ 500 μ m size with an optical microscope at magnification of 500. As a result of analyzing, the number of detected pores was 9pieces/mm² per unit area. The pore area ratio was 0.03%.

[0061] Compared with the results of using the titanium chips of Example 2, the results of using the chips of the Ti-Al-V alloys of Example 3 and Example 4 were equivalent. Therefore, it is considered that the method for producing the titanium powder according to the present embodiment is also suitable for producing the titanium alloy powder.

[Comparative Example 1]

[0062] Titanium powder was produced using the sponge titanium having the inner MgCl₂ concentration of 0.2 mass% as a titanium raw material, otherwise under the same conditions as in Example 1. The total MgCl₂ concentration of the sponge titanium was 0.3 mass%. Titanium powder was embedded in resin, polished cross-section of the sample, and observed at 16 locations of arbitrary locations of 700 μ m $\times$ 500 μ m size with an optical microscope at magnification of 500. The number of pores and area ratio were analyzed, and the detected pores were 85pieces/mm² per unit area. The pore area ratio was 0.7%.

[Comparative Example 2]

[0063] Purchasing the titanium powder produced by the gas atomization method having the same particle diameter as in Example 1. Titanium powder was embedded in the resin, polished the cross-section of the sample, and observed at 16 locations of arbitrary locations of 700 μ m $\times$ 500 μ m size with an optical microscope at magnification of 500. The

number of pores and area ratio were analyzed, and the detected pores were 130pieces/mm² per unit area. The pore area ratio was 1.0% (FIG.5).

Claims

1. A titanium-based powder comprising a ratio of a pore area obtained by dividing a cross-sectional area of pores in a cross-section of the titanium-based powder by an area of the cross-section of the titanium-based powder is 0.3% or less.
2. The titanium-based powder according to claim 1, wherein the titanium-based powder is an HDH powder.
3. A method for producing a titanium-based powder comprising a Hydrogenation-DeHydrogenation method including a hydrogenation process, a pulverization process, and a dehydrogenation process using a titanium-based raw material;
wherein a concentration of total MgCl₂ contained in the titanium-based raw material is 1.0 mass % or less, and a concentration of internal MgCl₂ contained in the titanium-based raw material is 0.1 mass % or less.
4. The method for producing the titanium-based powder according to claim 3, wherein the titanium-based raw material has a maximum thickness of 20 mm or less.
5. The method for producing the titanium-based powder according to claim 3 or claim 4, wherein a hydrogenated titanium-based powder is pulverized to have a D95 particle size of 300 μm or less in the pulverizing process.
6. The method for producing the titanium-based powder according to any of claims 3 to 5, wherein the titanium-based raw material is hydrogenated within a temperature range of 716°C or more and 1050°C or less over a period of 90 minutes or more in the hydrogenation process.

FIG. 1

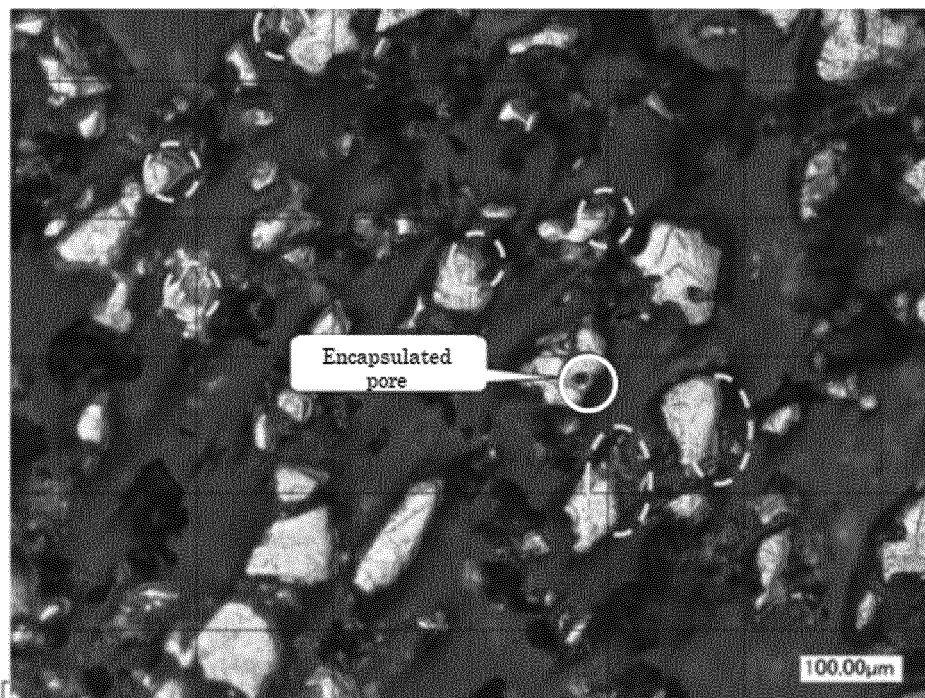


FIG. 2

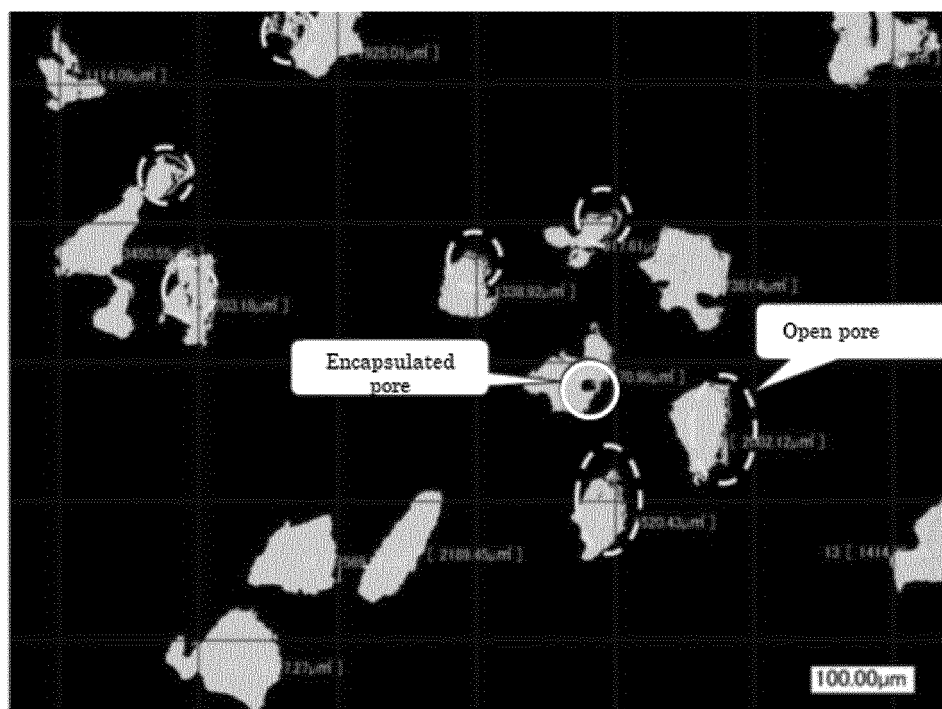


FIG. 3

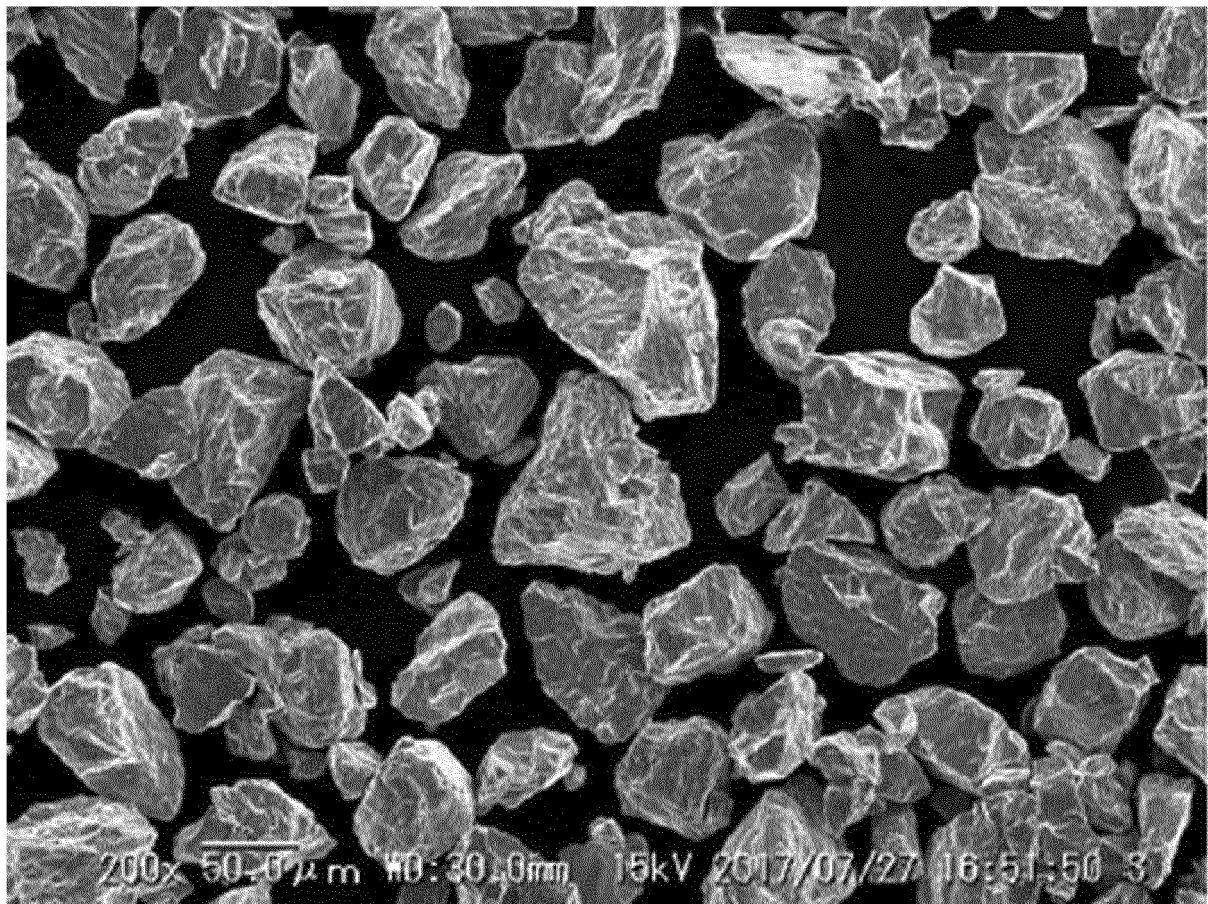


FIG. 4

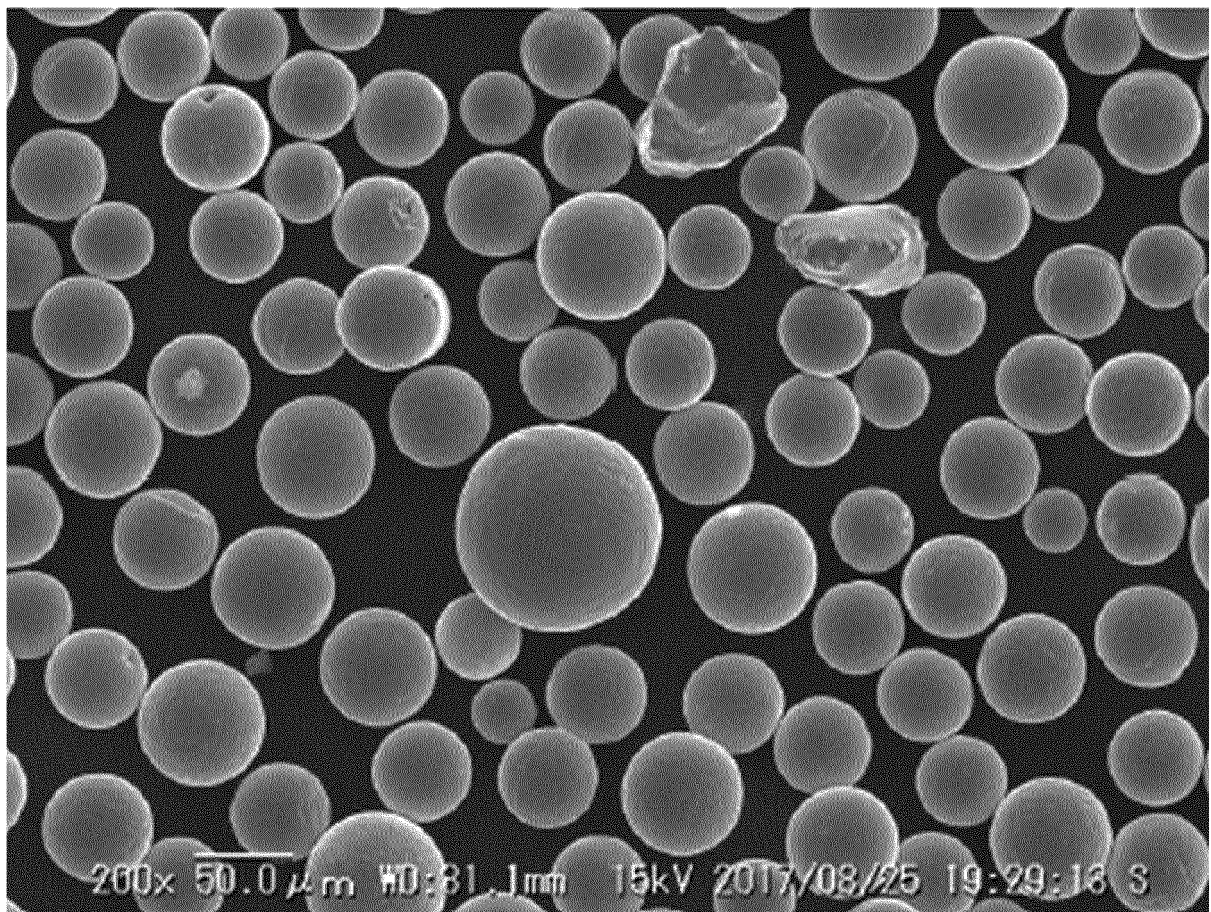
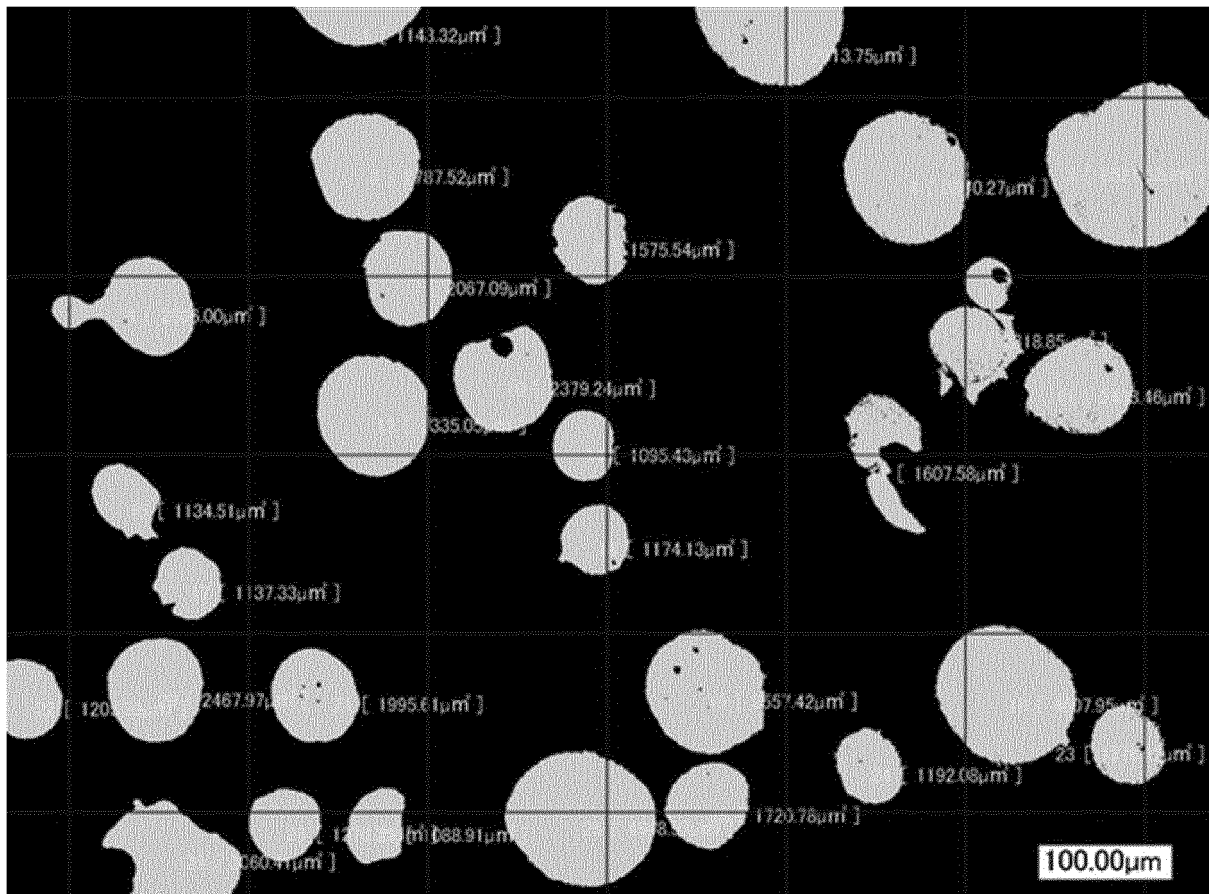


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/008968

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B22F1/00 (2006.01) i, B22F9/04 (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)

Int.Cl. B22F1/00, B22F9/04

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

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.
Y A	JP 1-139706 A (NIPPON STEEL CORP.) 01 June 1989, claims, page 2, upper right column, line 14 to page 4, upper right column, line 13, tables 1, 2 (Family: none)	1, 2 3-6
Y A	JP 2013-112878 A (TOHO TITANIUM CO., LTD.) 10 June 2013, paragraphs [0005]-[0010], [0022]-[0028] (Family: none)	1-5 6
Y	JP 2001-262246 A (TOHO TITANIUM CO., LTD.) 26 September 2001, claims, paragraphs [0025]-[0032] (Family: none)	3-5
A	JP 5-93213 A (SUMITOMO SITIX CORP.) 16 April 1993, paragraphs [0024], [0025] (Family: none)	1-6



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search
20 May 2019 (20.05.2019)Date of mailing of the international search report
28 May 2019 (28.05.2019)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP H05247503 B [0004]
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