



(11) **EP 4 825 509 A1**

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

(43) Date of publication:
21.10.2026 Bulletin 2026/43

(21) Application number: **24903254.1**

(22) Date of filing: **29.08.2024**

(51) International Patent Classification (IPC):
B22F 7/06 ^(2006.01) **B22F 1/00** ^(2022.01)
B22F 3/00 ^(2021.01) **B22F 3/02** ^(2006.01)
B22F 3/11 ^(2006.01) **C22C 1/08** ^(2006.01)
C25B 11/031 ^(2021.01)

(52) Cooperative Patent Classification (CPC):
B22F 1/00; B22F 3/00; B22F 3/02; B22F 3/11;
B22F 7/04; B22F 7/06; C22C 1/08; C25B 11/031

(86) International application number:
PCT/JP2024/031074

(87) International publication number:
WO 2025/126591 (19.06.2025 Gazette 2025/25)

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

(30) Priority: **15.12.2023 JP 2023212466**

(71) Applicant: **Toho Titanium CO., LTD.**
Chigasaki-shi
Kanagawa 253-8510 (JP)

(72) Inventors:
• **TAKADA, Motomu**
Chigasaki-shi, Kanagawa 253-8510 (JP)
• **INOUE, Yosuke**
Chigasaki-shi, Kanagawa 253-8510 (JP)
• **NAGANUMA, Noriyuki**
Chigasaki-shi, Kanagawa 253-8510 (JP)

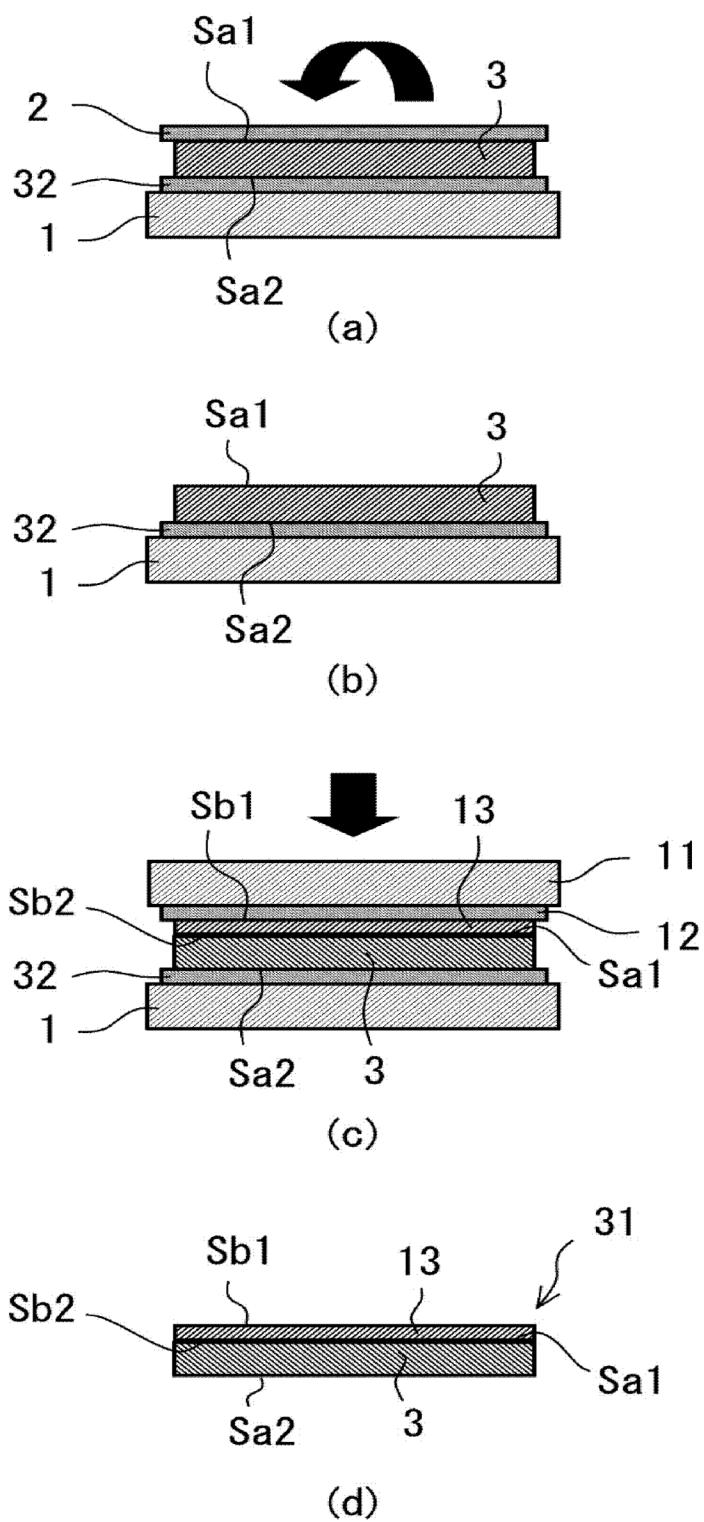
(74) Representative: **Mewburn Ellis LLP**
Aurora Building
Counterslip
Bristol BS1 6BX (GB)

(54) **METHOD FOR PRODUCING TITANIUM MOLDED BODY, METHOD FOR PRODUCING TITANIUM POROUS BODY, AND TITANIUM POROUS BODY**

(57) The method for producing a titanium formed body according to this invention is a method for producing a sheet-shaped titanium formed body, the method including a joining step of laminating multiple sheet-shaped dried bodies, each obtained by drying a paste

containing titanium powder, an organic binder, and an organic solvent, and heating the laminated bodies to a temperature of 70°C or higher and 200°C or lower while applying a pressure of 0.1 N/cm² or more in the thickness direction.

[Fig. 2]



Description

[Technical Field]

- 5 **[0001]** This invention relates to a method for producing a sheet-shaped titanium formed body, a method for producing a titanium porous body, and a titanium porous body.

[Background Art]

- 10 **[0002]** A titanium porous body produced by sintering titanium powder has gas and liquid permeability due to its pores, and electrical conductivity, as well as high corrosion resistance due to formation of a passive film on its surface or the like.

- [0003]** A titanium porous body having such properties has been studied for use as a porous transport layer (PTL) or the like in an environment where corrosion may occur in a polymer electrolyte membrane (PEM) type water electrolysis device. In particular, hydrogen produced by water electrolysis devices such as the PEM type using electricity derived from renewable energy sources is referred to as "green hydrogen", attracting increasing attention in recent years as efforts toward achieving a decarbonized society accelerate.

- [0004]** As for arts related to titanium porous bodies, for example, Patent Literature 1 describes "a method for producing a porous metal laminate including multiple layers having a porous layer in which multiple polyhedral voids, each having edges formed by the skeleton of a metal sintered body, are formed in a continuous state to each other, the method including: a lamination step of laminating the porous layer with an adjacent layer made of metal; and a fusion-cutting step of fusion-cutting the porous layer and the adjacent layer, which have been laminated, into a desired shape using a laser, wherein the fusion-cutting step, the porous layer and the adjacent layer are melted and solidified by the laser, thereby forming a fusion-bonded layer on the side surfaces of the porous layer and the adjacent layer to join the porous layer and the adjacent layer".

- [0005]** Furthermore, Patent Literature 2 describes "a composite material comprising a first region formed of a metal foam having a conductive metal component with a conductivity of 8 MS/m or more at 20°C, and a second region formed of a metal foam having a soft magnetic metal component".

- 30 [Citation List]

[Patent Literature]

[0006]

35

[PTL 1] Japanese Patent Application Publication No. 2011-106023 A

[PTL 2] Japanese Patent Application Publication No. 2021-529891 A

[Summary of Invention]

40

[Technical Problem]

- [0007]** When a titanium porous body is used as a porous transport layer in a PEM-type water electrolysis device, the titanium porous body may be incorporated while being pressed against the electrolyte membrane. In such a case, if the pores on the surface of the titanium porous body are large, the electrolyte membrane pressed against the porous body may partially enter those pores, causing significant deformation in the vicinity of the pores and potentially damaging the electrolyte membrane.

- [0008]** Therefore, from the viewpoint of suppressing damage to the electrolyte membrane, it is desirable that the titanium porous body have small pores opening on the surface facing the electrolyte membrane. Even if the pores on the surface are small, sufficient gas or liquid permeability can be achieved when the number of pores is large.

- [0009]** However, if the pores are small not only on the surface but throughout the entire titanium porous body, it may not be possible to achieve the required level of air permeability or liquid permeability, even if the number of pores is large. To address this, it is conceivable to produce a titanium porous body having a higher porosity by laminating multiple porous layers, positioning a porous layer with small pores on one surface side to suppress damage to the electrolyte membrane, while ensuring that the body as a whole exhibits good air permeability or liquid permeability.

- [0010]** In producing a titanium porous body including multiple porous layers, if multiple titanium sintered bodies intended to form the porous layers are laminated and joined by heating, each porous layer making up the titanium porous body is subjected to relatively high-temperature heating twice: the heating for sintering during the production of

the titanium sintered bodies and the heating during joining. As a result, the titanium porous body obtained by joining multiple titanium sintered bodies may have smaller pores as a whole, and may not achieve the expected excellent level of air permeability or liquid permeability. This applies not only to the production of titanium porous bodies including multiple porous layers with varying pore sizes and numbers, but also to the production of titanium porous bodies including multiple porous layers with similar pore sizes and numbers.

[0011] An object of this invention is to provide a method for producing a titanium formed body capable of being used to produce a titanium porous body having multiple porous layers and a relatively high porosity, a method for producing a titanium porous body, and a titanium porous body.

[Solution to Problem]

[0012] As a result of intensive studies, the inventors have conceived of laminating multiple sheet-shaped dried bodies obtained by drying a titanium powder paste and joining them under predetermined conditions. By performing debinding and sintering on the resulting titanium formed body, the number of high-temperature heating cycles can be reduced compared to joining pre-sintered bodies. As a result, the titanium porous body finally produced has a relatively high porosity.

[0013] The method for producing a titanium formed body according to this invention is a method for producing a sheet-shaped titanium formed body, the method including a joining step of laminating multiple sheet-shaped dried bodies, each obtained by drying a paste containing titanium powder, an organic binder, and an organic solvent, and heating the laminated bodies to a temperature of 70°C or higher and 200°C or lower while applying a pressure of 0.1 N/cm² or more in the thickness direction.

[0014] The above method for producing a titanium formed body may include, prior to the joining step, a drying step of drying the paste to obtain sheet-shaped dried bodies.

[0015] In the drying step, the paste may be heated to a temperature of 90°C or higher and 165°C or lower.

[0016] The drying of the paste in the drying step may be performed on a resin substrate.

[0017] In the joining step, the laminated sheet-shaped dried bodies may be subjected to pressure and heating while being sandwiched between molds from both sides in a thickness direction.

[0018] In this case, it is preferable to perform the pressure and heating in the joining step with a resin substrate interposed between the sheet-shaped dried bodies and the molds.

[0019] It is preferable that the average particle diameter of the titanium powder in at least one of the sheet-shaped dried bodies be 10 μm or more and 20 μm or less.

[0020] It is preferable that the difference between the average particle diameter of the titanium powder in the sheet-shaped dried body on one surface side and the average particle diameter of the titanium powder in at least one other sheet-shaped dried body be 5 μm or more.

[0021] It is preferable that the paste used to produce the sheet-shaped dried bodies does not contain a foaming agent.

[0022] The method for producing a titanium porous body according to this invention is a method for producing a sheet-shaped titanium porous body, the method including: a debinding step of heating a titanium formed body produced by any of the above methods for producing a titanium formed body to volatilize the organic binder in the titanium formed body; and a sintering step of heating the titanium formed body after the debinding step to sinter the titanium powder in the titanium formed body.

[0023] The titanium porous body according to this invention is in a sheet-shaped, the titanium porous body including multiple layers of titanium porous layers, each having pores through which a gas and/or liquid can pass, wherein adjacent titanium bonding surfaces in a thickness direction are bonded and laminated to one another, and wherein an average area of the pores opening on a surface of the porous layer forming one surface of the multiple porous layers is 5 μm² or more and 15 μm² or less, a standard deviation of areas of the pores is 35 μm² or less, a number of the pores present within a rectangular region having an area of 22,000 μm² and an aspect ratio of 4:3 is 256 or more, and the overall porosity including the multiple porous layers is 40% or more and 60% or less.

[0024] It is preferable that the average area of the pores opening on the other surface located on the reverse side of the one surface be 1.5 times or more the average area of the pores opening on the one surface.

[0025] The total thickness is preferably 200 μm or more and 3,000 μm or less.

[0026] The thickness of the porous layer making up one surface side is preferably 30% or less of the total thickness.

[Advantageous Effects of Invention]

[0027] According to the method for producing a titanium formed body of this invention, it is possible to produce a titanium formed body that can be used to produce a titanium porous body having multiple porous layers and a relatively high porosity.

[Brief Description of Drawings]

[0028]

[Fig. 1] Figs. 1(a) and 1(b) are cross-sectional views along a thickness direction, each showing a sheet-shaped dried body that can be used in the method for producing a titanium formed body according to an embodiment of this invention.

[Fig. 2] Figs. 2(a) to 2(d) are cross-sectional views illustrating an example of a procedure for joining the sheet-shaped dried bodies shown in FIG. 1.

[Description of Embodiments]

[0029] Embodiments of the present invention will be described in detail below.

[0030] The method for producing a titanium formed body according to one embodiment of this invention includes a joining step of laminating and joining multiple sheet-shaped dried bodies.

[0031] To obtain each sheet-shaped dried body, a paste preparation step of mixing titanium powder, an organic binder, and an organic solvent, and a drying step of forming the paste into a sheet and drying it, can be performed. In the joining step, the laminated multiple sheet-shaped dried bodies are heated to a temperature of 70°C or higher and 200°C or lower while being pressed in the thickness direction with a pressure of 0.1 N/cm² or more. As a result, the multiple sheet-shaped dried bodies are joined together to form a titanium formed body.

[0032] The titanium formed body described above is sequentially subjected to a debinding step and a sintering step, resulting in a titanium porous body. Because the titanium porous body was formed by laminating and joining multiple sheet-shaped dried bodies in the joining step during production, it includes titanium porous layers each serving as a sintered body of each sheet-shaped dried body. By appropriately setting the particle diameter of the titanium powder and other conditions used to form the sheet-shaped dried bodies, the titanium porous body can be such that, for example, when used as a porous transport layer within a PEM-type water electrolysis device, the pores on the surface against which the electrolyte membrane is pressed are small, while the body as a whole has a relatively high porosity.

[0033] The titanium porous body produced as described above has a relatively high porosity compared to one produced by joining titanium sintered bodies, because it is subjected to high-temperature heating fewer times, such as during sintering. In other words, when debinding and sintering are performed on each of multiple sheet-shaped dried bodies, and the resulting multiple titanium sintered bodies are heated and joined, high-temperature heating takes place at least twice during sintering and joining, resulting in advanced sintering of the titanium powder and a decrease in porosity and the like. In contrast, according to the embodiment described herein, the number of high-temperature heating cycles can be reduced, thereby enabling the production of, for example, a titanium porous body having a high porosity.

(Paste Preparation Step)

[0034] In the paste preparation step, raw materials containing titanium powder, an organic binder, and an organic solvent are mixed using a mixer equipped with a stirrer, a rotary mixer, a three-roll mill, or the like, to prepare a paste. At this time, pulverization may also be performed using a vibration mill, bead mill, or other pulverizing mixer.

[0035] As titanium powder, ground powders such as hydrogenation-dehydrogenation (HDH) titanium powder or titanium hydride powder, as well as spherical powders such as atomized powder, can be used. For example, when fine titanium powder having an average particle diameter of 10 μm or more and 20 μm or less is used, the porous layer obtained by sintering the sheet-shaped dried body will have small pores. On the other hand, when coarse titanium powder having an average particle diameter exceeding 20 μm is used, the pores in the porous layer after sintering become larger, resulting in a higher porosity.

[0036] From the perspective of producing a titanium porous body having small pores opening on one surface but a high overall porosity, the difference between the average particle diameter of the titanium powder used to produce one sheet-shaped dried body that will become the porous layer positioned on one surface side and the average particle diameter of the titanium powder used to produce at least one other sheet-shaped dried body is preferably 5 μm or more, and more preferably 10 μm or more. However, since an excessively large difference between the average particle diameters may cause the difference in sintering shrinkage between the sheet-shaped dried bodies to become excessively large, which may lead to separation of the titanium porous layers, this difference may be limited to 100 μm or less, and further to 50 μm or less, taking this into consideration.

[0037] The above average particle diameter refers to a particle diameter at which the cumulative distribution on a volume basis reaches 50% in the particle size distribution obtained by laser diffraction scattering.

[0038] As the organic binder used for the paste, various binders can be appropriately selected as needed. Examples

include methyl cellulose-based, polyvinyl alcohol-based, ethyl cellulose-based, acrylic-based, and polyvinyl butyral-based binders. Organic binders exhibiting hydrophobic properties are preferred. However, the examples are not limited to those listed here. The organic solvent may be, for example, an alcohol such as ethanol, isopropyl alcohol, terpeneol, or butyl carbitol. As an example, the organic binder may be polyvinyl butyral and the organic solvent may be isopropyl alcohol. The paste may further contain a plasticizer such as glycerin or ethylene glycol, and/or a surfactant such as an alkylbenzene sulfonate.

[0039] Preferably, the paste does not contain water as a solvent. It is also preferable that the paste does not contain a foaming agent. It should be noted that it is sufficient for the paste to be free of water as a solvent, and the inclusion of water that may unintentionally enter the paste, such as through moisture absorption, is permissible. When a paste containing water and/or a foaming agent is used to produce a titanium porous body, larger pores are formed during the production process, making it impossible to achieve the desired pore size. If a titanium porous body with large pore sizes is produced using a paste containing water and/or a foaming agent, the resulting titanium porous body will have poor surface smoothness that is prone to damaging the electrolyte membrane in a solid polymer-type water electrolysis device.

(Drying Step)

[0040] In the drying step, the above paste is applied in a relatively thin sheet form and heated. As a result, mainly the organic solvent in the paste evaporates, and a sheet-shaped dried body is obtained.

[0041] The paste can be applied to a flat surface such as a table, but it is preferable to apply it to a resin substrate. The resin substrate onto which the paste is applied may be placed on the mold described below, but is not limited thereto. It should be noted that if the paste is applied directly onto a graphite mold, carbon from the mold may mix into the paste or the sheet-shaped dried body during the drying step, which may cause the titanium porous body to become discolored after the sintering step. Resin substrates are relatively inexpensive and easy to handle due to their flexibility. Specific examples of resin substrate materials include polyesters such as PET (polyethylene terephthalate) and PEN (polyethylene naphthalate), and polyvinyl compounds such as polyethylene, polypropylene, polystyrene, and polyvinyl alcohol. Among these, PET resin substrates are inexpensive, and the sheet-shaped dried body can be easily separated from the resin substrate after the drying step.

[0042] If necessary, a release layer may be provided on the resin substrate. When providing the release layer, a silicone coating or the like can be used as the release layer. For example, the release layer can be provided on the substrate by selecting a substrate on which a material such as CERAPEEL (registered trademark) manufactured by Toray Industries, Inc. has been pre-applied. The provision of the release layer on the substrate makes it possible to easily separate the resulting thin sheet-shaped dried body from the substrate after the drying step.

[0043] The heating temperature during drying can be 90°C or higher and 165°C or lower. When the paste is dried at a temperature within this range, drying can be completed in a relatively short period of time while suppressing boiling of the organic solvent and other components in the paste. The drying time is not particularly limited and may be determined as appropriate, for example, it can be 5 minutes or more and 300 minutes or less. Drying is preferably performed in an oxygen-containing atmosphere, for example, in an air atmosphere. This makes it possible to suppress an increase in production cost.

[0044] When producing a titanium porous body including multiple porous layers having differing thicknesses, the thickness of the paste coating can be adjusted during the preparation of each sheet-shaped dried body in accordance with the thickness of the above porous layers.

[0045] For example, in Figs. 1(a) and 1(b), respectively, by adjusting the thickness of the paste applied to the resin substrates 2, 12 placed on molds 1, 11 and drying them, a sheet-shaped dried body 3 having a thickness T_a and a sheet-shaped dried body 13 having a thickness T_b thinner than T_a are obtained.

[0046] For the relatively thick sheet-shaped dried body 3 having thickness T_a , titanium powder with a relatively large average particle diameter may be used to increase the overall porosity of the titanium porous body. Furthermore, the relatively thin sheet-shaped dried body 13 having a thickness T_b may be used as the porous layer forming the surface against which the electrolyte membrane is pressed in a PEM-type water electrolysis device, and titanium powder with a relatively small average particle diameter may be used.

[0047] The molds 1, 11 may only possess the required heat resistance and have a flat surface in contact with the resin substrates 2 and 12 or the paste or sheet-shaped dried bodies 3 and 13, and those with excellent heat transfer properties are preferred. Specific examples of molds 1, 11 include graphite setters. Although the molds 1, 11 are used herein as an example, it is possible to produce titanium formed bodies without using molds 1, 11, and various known techniques can be adopted for applying the paste. For example, although not shown in the figures, a method (so-called comma coating method) may be adopted in which a long resin substrate is fed by a roll, and paste is dispensed onto the resin substrate from a space between that the roll and a paired roll, thereby continuously coating the paste onto the resin substrate. Alternatively, although also not shown in the figures, a doctor blade method may be adopted.

(Joining Step)

[0048] In the joining step, multiple sheet-shaped dried bodies are joined by heating while applying pressure in the thickness direction in a laminated state. This results in a titanium formed body.

[0049] At this time, the pressure applied in the thickness direction to the multiple sheet-shaped dried bodies laminated together is 0.1 N/cm² or more, and preferably 0.2 N/cm² or more and 5.0 N/cm² or less. Furthermore, the heating temperature is 70°C or higher and 200°C or lower, and preferably 100°C or higher and 180°C or lower.

[0050] If the heating temperature is too low or the pressure is too small, there is a concern that the multiple sheet-shaped dried bodies will not be sufficiently joined to one another. In such cases, in severe instances, the sheet-shaped dried bodies of the titanium formed body may be partially separated from one another after the joining step or after the debinding step described below. It is considered that good joining can be achieved by applying a predetermined amount of pressure while maintaining the temperature at a sufficiently high level, as the organic binder in each sheet-shaped dried body softens during compression. On the other hand, by not applying excessive pressure, it is possible to effectively suppress distortions in the dimensions and shape of the sheet-shaped dried bodies caused by compression during pressurization. Furthermore, higher heating temperatures tend to allow the joining of multiple sheet-shaped dried bodies to be completed in a shorter period of time. However, if the heating temperature is too high, there is a concern that the titanium formed body will dry out excessively and crack, or that the titanium formed body will deform in response to the deformation of the resin substrate.

[0051] Pressurization and heating during the joining step can be performed with the laminated sheet-shaped dried bodies sandwiched between the molds from both sides in the thickness direction. This ensures the flatness of the titanium formed body. Preferably, the state of being sandwiched between the molds is maintained until the temperature decreases to room temperature after heating. The molds may be the same as those used in the drying step described above, but are not limited thereto. Furthermore, the molds may only have a flat surface on the side facing the sheet-shaped dried bodies so that the titanium formed body described below can be formed into a sheet shape, and the shape of the other parts is not particularly restricted. When using molds in the joining step, the pressure described above is applied to the sheet-shaped dried bodies, taking into account the pressure exerted by the weight of the molds themselves. In other words, the pressure applied to the sheet-shaped dried bodies includes that exerted by the weight of the molds themselves.

[0052] When using molds in the joining step, it is preferable to perform pressurization and heating with a resin substrate interposed between the sheet-shaped dried bodies and the molds in order to suppress contamination from the molds to the sheet-shaped dried bodies during heating at the time of joining. This resin substrate may be the same as that used in the drying step described above, but a different one may also be used.

[0053] As shown in Fig. 1, the sheet-shaped dried bodies 3, 13 tend to have a surface roughness at surfaces Sa1 and Sb1 on the resin substrate 2, 12 side positioned there during the drying step, that is smaller than the surface roughness at surfaces Sa2, Sb2 on the reverse side. For this reason, it is preferable to join the sheet-shaped dried body 13 for the porous layer that forms the surface against which the electrolyte membrane is pressed in the titanium porous body, to the sheet-shaped dried body 3 such that the surface Sb1 on the resin substrate 12 side faces outward in the thickness direction of the titanium formed body.

[0054] In contrast, even if one attempts to join the surface Sa2 that is on the reverse side of the sheet-shaped dried body 3 for the porous layer forming the other surface of the titanium porous body, and that was positioned on the resin substrate 2 side, to the reverse surface Sb2 of the sheet-shaped dried body 13, a sufficiently strong joining cannot be achieved in some cases due to the coarse surface roughness of both surfaces Sa2 and Sb2. Therefore, it is preferable to join surface Sa1 located on the resin substrate 2 side of the sheet-shaped dried body 3, to the reverse surface Sb2 of the sheet-shaped dried body 13.

[0055] Fig. 2 illustrates an example of joining sheet-shaped dried bodies 3, 13 by laminating them. Here, first, the sheet-shaped dried body 3, after undergoing the drying step, is temporarily peeled away from the mold 1 together with the resin substrate. Then, as shown in Fig. 2(a), another resin substrate 32 is placed on the mold 1, and the sheet-shaped dried body 3 is positioned on top of that resin substrate 32 in such an orientation that the surface Sa2 that is on the reverse side of the surface Sa1 located on the resin substrate 2 side of the sheet-shaped dried body 3 contacts the resin substrate 32. In other words, as indicated by the arrows in the figure, the sheet-shaped dried body 3, with the resin substrate 2 still adhered to it, is turned over and placed on the other resin substrate 32.

[0056] Next, as shown in Fig. 2(b), the resin substrate 2 used in the drying step is peeled off from the sheet-shaped dried body 3 to expose the surface Sa1 that was located on the resin substrate 2 side of the sheet-shaped dried body 3.

[0057] Thereafter, as shown in Fig. 2(c), the sheet-shaped dried body 13 is placed on top of the sheet-shaped dried body 3 together with the resin substrate 12 and the mold 11, such that the reverse surface Sb2 of the sheet-shaped dried body 13, which is on the opposite side from the surface Sb1 on the resin substrate 12 side, faces the exposed surface Sa1 that was located on the resin substrate 2 side of the sheet-shaped dried body 3. It should be noted that

the resin substrate 12 is often not adhered to the mold 11, and in this case, the sheet-shaped dried body 13 and the resin substrate 12 may first be placed on the sheet-shaped dried body 3, and then the mold 11 may be placed on top of them to achieve the arrangement shown in Fig. 2(c). At this stage, the mold 11 may be replaced with a mold different from the one used in the drying step. In this state, the sheet-shaped dried bodies 3, 13 are pressed and heated as indicated by the arrows in the figure, thereby joining them together. As a result, a titanium formed body 31 having the sheet-shaped dried bodies 3, 13 joined together is obtained, as shown in Fig. 2(d).

[0058] When the joining step is performed as shown in Figs. 2(a) to 2(d), for example, the surface Sb1 on the resin substrate 12 side of the sheet-shaped dried body 13, which uses fine titanium powder and has the smallest surface roughness, becomes one surface of the titanium formed body 31. The other surface of the titanium formed body 31 is the reverse surface Sa2 of the sheet-shaped dried body 3, which uses coarse titanium powder and has the highest surface roughness. Since the reverse surface Sb2 of the sheet-shaped dried body 13 contacts the surface Sa1 on the resin substrate 2 side of the sheet-shaped dried body 3, which does not have a particularly high surface roughness, the sheet-shaped dried body 3 and the sheet-shaped dried body 13 can be firmly joined.

[0059] Although not shown in the figures, a titanium formed body may be produced by laminating and joining three or more sheet-shaped dried bodies. Furthermore, while this description has focused on an example where the resin substrate 2 used in the drying step, or a resin substrate 32 made of the same material, is also used in the joining step, resin substrates with different materials or properties may be used in the drying and joining steps. The properties required for the resin substrate in the drying step include preventing the paste from detaching from the resin substrate during application and allowing the sheet-shaped dried body to be relatively easily separated from the resin substrate after drying. On the other hand, in the joining step, a resin substrate is required that allows the titanium formed body to be separated relatively easily and that possesses heat resistance at a predetermined temperature.

[0060] In the joining step, the sheet-shaped dried body (corresponding to sheet-shaped dried body 3 in FIG. 2) to which the sheet-shaped dried body forming one surface of the titanium formed body (corresponding to sheet-shaped dried body 13 in Fig. 2) is to be joined preferably has a surface roughness Ra on the surface Sa1 of 3.0 μm or less, more preferably 0.1 μm or more and 3.0 μm or less, and even more preferably 0.2 μm or more and 2.0 μm or less. If the surface roughness Ra falls within this range, the surface Sa1 of the sheet-shaped dried body 3 is smooth, allowing for a larger bonding area with the sheet-shaped dried body 13 and enabling good adhesion between the sheet-shaped dried bodies. The Surface roughness Ra refers to the arithmetic mean roughness and is measured in accordance with ISO 4287: 1997. For this measurement, a roughness measuring instrument manufactured by Mitutoyo Corporation (Model No.: SJ-210) may be used.

(Debinding Step)

[0061] When producing a titanium porous body, the above titanium formed body may be subjected to a debinding step. In the debinding step, for example, the resin substrate used in the above joining step is removed, and the titanium formed body is heated, in some cases while placing it on a mold, to volatilize primarily the organic binder within the titanium formed body. When performing the debinding step on a mold, for example, the titanium formed body 31 obtained in Fig. 2(d) can be placed on one of the molds 1, 11 and subjected to the debinding step, and in this case, the other mold need not be used. The debinding step does not require the titanium formed body to be sandwiched between molds, as in the joining step.

[0062] In the debinding step, it is preferable, for example, to heat the titanium formed body to a temperature of 300°C or higher and 450°C or lower. This allows the organic binder to be removed while suppressing the sintering of the titanium powder caused by heating.

[0063] The heating time is not particularly limited, but may be set to a period of 3 hours or more and 20 hours or less, or 3 hours or more and 12 hours or less. The atmosphere during heating may be an oxygen-containing atmosphere, such as an air atmosphere. When using an oxygen-containing atmosphere, it is possible to suppress the increase in costs associated with strictly controlling the atmosphere.

(Sintering Step)

[0064] Subsequently, a sintering step is performed on the titanium formed body that has undergone the debinding step to sinter the titanium powder in the formed body. After the sintering step, a titanium porous body is obtained as a sintered body.

[0065] In the sintering step, the titanium formed body after the debinding step may be heated to a temperature of, for example, 700°C or higher and 1,100°C or lower, typically 825°C or higher and 950°C or lower. The above temperature may be maintained for a period of 1 hour or more and 4 hours or less. The atmosphere during sintering may be, for example, a vacuum or reduced-pressure atmosphere of 1.0×10^{-2} Pa or less, or an inert gas atmosphere of Ar or He.

(Titanium Porous Body)

[0066] The sheet-shaped titanium porous body produced by the production method described above includes multiple layers of titanium porous layers formed after debinding and sintering of the above multiple laminated sheet-shaped dried bodies. The multiple porous layers are laminated such that the titanium bonding surfaces adjacent to each other in the thickness direction are bonded together, and each layer has pores and is permeable to a gas and/or a liquid.

[0067] When the titanium porous body is produced using the above production method, the titanium powder located on the adjacent surfaces of each sheet-shaped dried body undergoes sintering to form titanium bonding surfaces that are bonded to each other. If adjacent sheet-shaped dried bodies are produced using titanium powders with different average particle diameters, the sheet-shaped titanium porous body obtained after the sintering step exhibits regions where the size of the skeleton formed by the bonded titanium powder varies in the thickness direction when viewed from the side, and it can be observed that the above titanium bonding surfaces are located in these regions. It is preferable that the titanium bonding surfaces of the multiple porous layers contain substantially no metals other than titanium or compounds that do not contain titanium, as this enables the achievement of the required high electrical conductivity at low cost. Furthermore, titanium porous bodies used as porous transport layers in PEM-type water electrolysis devices may be those through which a gas and/or a liquid can permeate in directions other than the thickness direction, such as directions perpendicular to the thickness direction.

[0068] Each porous layer has a skeleton formed by the bonding of titanium powder particles and has a sponge-like three-dimensional mesh structure in which pores are formed between the mutually bonded titanium powder particles.

[0069] One surface of the titanium porous body is formed by the porous layer making up the portion on one surface side (also referred to as the "one-side porous layer"). In other words, one surface corresponds to the surface of the one-side porous layer.

[0070] The average area of the pores opening on one surface of the titanium porous body is $5 \mu\text{m}^2$ or more and $15 \mu\text{m}^2$ or less. If the pores on one surface have a relatively small area as described above, that surface can generally be considered smooth, and damage to the electrolyte membrane within a PEM-type water electrolysis device can be effectively suppressed.

[0071] From this perspective, it is preferable that the average area of the pores on one surface be $7 \mu\text{m}^2$ or more and $13 \mu\text{m}^2$ or less. If the average pore area on one surface is too small, there is a risk that air permeability or liquid permeability will decrease. Furthermore, if the average pore area on one surface is too large, the electrolyte membrane may partially enter the pores, causing significant deformation in positions adjacent to those pores and potentially leading to damage to the electrolyte membrane.

[0072] From a similar perspective, the standard deviation of the pore area on that surface is preferably $35 \mu\text{m}^2$ or less, more preferably $3 \mu\text{m}^2$ to $25 \mu\text{m}^2$, and particularly preferably $5 \mu\text{m}^2$ to $17 \mu\text{m}^2$. A small standard deviation means that many of the pores present on one surface are of the required fine size.

[0073] Furthermore, the number of pores present within a rectangular region on one surface having an area of $22,000 \mu\text{m}^2$ and an aspect ratio of 4:3 is 256 or more, preferably 290 or more, and more preferably 400 or more. The presence of a large number of such fine pores on one surface allows for the achievement of smoothness while ensuring the required air permeability or liquid permeability. The number of pores within the rectangular region on one surface is not limited to this, but may, for example, be 700 or fewer, or 550 or fewer.

[0074] The other surface of the titanium porous body refers to the surface located on the reverse or opposite side of the one surface, and is formed by the porous layer making up the other surface side (also referred to as the "other-side porous layer"). In other words, the other surface corresponds to the surface of the other-side porous layer.

[0075] To enhance the air permeability or liquid permeability of the titanium porous body, the average area of the pores opening on the other surface is preferably 1.5 times or more, and more preferably 3 times or more, the average area of the pores on one surface. By forming the other surface side from a porous layer having larger pores, a gas and/or a liquid can more easily flow through the interior of the titanium porous body. The upper limit of the average area of the pores opening on the other surface is not particularly limited, provided that the titanium porous body has the required strength to be incorporated and used in, for example, a PEM-type water electrolysis device. However, it may be set at 10 times or less, 7 times or less, or 5 times or less the average area of the pores on one surface.

[0076] The average value and standard deviation value of the areas of the pores opening on the surface, as well as the number of pores within a predetermined rectangular region, are measured using a scanning electron microscope (Keyence Corporation ultra-deep multi-angle lens VHX-D510). More specifically, for both the one surface and the other surface, SEM images are acquired at a magnification of $2,000\times$ for a rectangular region having an area of $22,000 \mu\text{m}^2$ and an aspect ratio of 4:3 on the respective surfaces. SEM image analysis is then performed using the scanning electron microscope, and half of the maximum detected luminance value of the SEM image is set as the threshold, and a closed region having a luminance in the range of 0 to the threshold value is regarded as one pore. At this time, a binarization process may be applied to the SEM image if necessary. After binarization, a small-particle removal process (processing of black pixels after binarization) is performed for closed regions of 50 pixels or less, followed by

a hole-filling process (processing of white pixels after binarization) for closed regions of 50 pixels or less. Using this data, the number and area of each pore are calculated, and the standard deviation value is obtained as the square root of the variance. Such SEM image analysis is performed for five rectangular regions on the surface that are at least partially offset from each other, and the average value of the pore areas and the average number of pores in those rectangular regions are taken as the average value of the pore areas, the standard deviation value, and the number of pores within the rectangular region on the surface, respectively. In the case where the surface of the titanium porous body is square or rectangular in plan view, the five rectangular regions described above are located at the center and at the four corners.

[0077] The thickness of the sheet-shaped titanium porous body (total thickness including all porous layers) may be 200 μm or more and 3,000 μm or less. For example, such a titanium porous body having a relatively large thickness may be required for the porous transport layer of a PEM-type water electrolysis device. On the other hand, if the thickness is too large, the PEM-type water electrolysis device may become larger in size. The thickness of the titanium porous body may be, for example, 200 μm or more, 1,000 μm or less, and further 500 μm or less.

[0078] The thickness of the titanium porous body is measured at five points: four at the periphery and one at the center of the titanium porous body, using, for example, a digital thickness gauge such as a Mitutoyo Corporation digital thickness gauge (Model No.: 547-321) having a flat-type probe with a diameter of $\Phi 10$ mm and a measurement accuracy of 0.01 mm, and the average of these measured values is taken as the average thickness. If the sheet-shaped titanium porous body is rectangular in plan view, the above four peripheral points correspond to the four corners.

[0079] In some cases, the thickness of the one-side porous layer is 20 μm or more and 120 μm or less, or 35 μm or more and 100 μm or less. In addition, the thickness of the one-side porous layer may be 30% or less, 20% or less, or further 15% or less of the total thickness described above. Since the one-side porous layer is composed of a porous layer having small pores, an excessive thickness may reduce the overall air permeability or liquid permeability of the titanium porous body. On the other hand, by increasing the thickness of the one-side porous layer to a certain extent, the corresponding porous layer can ensure sufficient strength after sintering during its production, and the porous layer becomes less susceptible to cracking when it is pressed against the electrolyte membrane together with other porous layers. The one-side porous layer preferably has the smallest thickness among the multiple porous layers. By making the one-side porous layer, which has small pores and is less permeable to gas or liquid, the thinnest, the air permeability or liquid permeability of the titanium porous body can be significantly improved.

[0080] The thickness of the other-side porous layer is preferably 100 μm to 2,900 μm , or 100 μm to 1,000 μm , or further 200 μm to 600 μm . By increasing the thickness of the other-side porous layer to a certain extent, the air permeability or liquid permeability can be further improved, and by avoiding excessive thickness, miniaturization of the water electrolysis device may be achieved and the electrolysis efficiency per unit area may be enhanced.

[0081] The thickness of each porous layer is measured by observing and measuring the thicknesses at five points on a cross-section in the thickness direction of a resin-embedded and polished titanium porous body using SEM, and the average value of these measurements is adopted. Since the functions required for each porous layer in the sheet-shaped titanium porous body according to this embodiment differ, portions where differences in the size of the skeleton formed by the bonded titanium powder can be observed in the lamination direction are identified, and the thickness of each porous layer is determined from SEM observations of those portions.

[0082] The surface area of the sheet-shaped titanium porous body in plan view can be appropriately determined depending on various conditions and is not particularly limited. For example, it may be 70 mm^2 or more and 600,000 mm^2 or less, or 10,000 mm^2 or more and 600,000 mm^2 or less. The term "sheet-shaped" refers to a plate-like or foil-like shape having a small thickness relative to its planar dimensions, and the planar shape is not particularly limited.

[0083] The titanium porous body may be composed of two porous layers in which the one-side porous layer and the other-side porous layer are directly bonded at their titanium bonding surfaces. Alternatively, one or more porous layers may be provided as an intermediate layer between the one-side porous layer and the other-side porous layer. In this case, the flow of a gas and/or a liquid within the titanium porous body can be controlled to some extent by gradually increasing the pore size.

[0084] The titanium porous body has an overall porosity, including the multiple porous layers, of 40% or more and 60% or less, and preferably 45% or more and 55% or less. If the porosity falls within this range, the titanium porous body possesses the required air permeability or liquid permeability for the intended application and can be effectively used as a porous transport layer in a solid polymer-type water electrolysis device. If the porosity is too high, there is concern that the mechanical strength of the titanium porous body will be insufficient, making it prone to unintended compressive deformation.

[0085] The porosity ε of the titanium porous body is calculated using the volume calculated from the external dimensions such as the width, length, and thickness of the titanium porous body, the apparent density ρ' calculated from the mass, and the true density ρ (4.51 g/cm^3) of titanium making up the titanium sintered body, according to the equation: $\varepsilon = (1 - \rho'/\rho) \times 100$.

[0086] The titanium porous body is made of titanium. When made of titanium, the titanium porous body can exhibit high electrical conductivity at an appropriate relative density. The titanium content of the titanium porous body (and further of each porous layer) is preferably 97 mass% or more, and more preferably 98 mass% or more. The upper limit of the titanium content may be, for example, 99.8 mass% or less, or 99 mass% or less, although not particularly limited thereto. The titanium content refers to the purity of titanium, taking into account not only metallic components but also impurity gas components such as oxygen. Therefore, the titanium content is determined by subtracting the total content of impurity components including metallic components and gas components, from 100 mass%.

[0087] The titanium porous body may have a purity corresponding to pure titanium grades 1 to 4, typically grades 1 to 2, as defined in JIS H 4600 (2012), except for the oxygen content. The oxygen content of the titanium porous body can be measured by the inert gas fusion-infrared absorption spectroscopy.

[Examples]

[0088] Next, the method for producing a titanium formed body and the method for producing a titanium porous body of this invention were experimentally carried out, and titanium porous bodies were produced on a trial basis, which are described below. However, descriptions herein are merely for illustrative purposes, and are not intended to be limited thereto.

(Example 1)

[0089] As shown in Table 1, titanium powder (hydrogenation-dehydrogenation (HDH) titanium powder) with an average particle diameter of 14 μm and titanium powder with an average particle diameter of 21 μm were each mixed with an organic solvent (isopropyl alcohol) and an organic binder (polyvinyl butyral) to prepare pastes containing these materials. It should be noted that the pastes did not contain water or foaming agents. Each paste was applied in a sheet-shape onto a PET resin substrate and heated at 150°C for 90 minutes to dry it, thereby obtaining sheet-shaped dried bodies. In addition, the PET resin substrate was provided with a silicone coating as a release layer.

[0090] Next, as shown in Fig. 2, the sheet-shaped dried body for the other-side porous layer was flipped over together with the resin substrate and placed on top of another resin substrate laid out on the mold. Then, the upper resin substrate was peeled off and removed, and the sheet-shaped dried body for the one-side porous layer was placed on top of it, flipped over together with the resin substrate. Furthermore, the mold was placed on top of this, and in this state, heating and pressurization were performed at the temperature, pressure, and time shown in Table 1. It should be noted that the pressure was applied to the sheet-shaped dried bodies by placing a weight on the upper mold. As a result, the sheet-shaped dried bodies were joined together to form a titanium formed body.

[0091] Next, the titanium formed body described above was heated in an air atmosphere at a temperature of 380°C for the duration shown in Table 1 to volatilize the organic binder and perform debinding. Subsequently, the debinded titanium formed body was heated under vacuum conditions at the temperature shown in Table 1 for one hour. As a result, the titanium powder in the titanium formed body was sintered, yielding a titanium porous body.

(Example 2)

[0092] As shown in Table 2, a titanium porous body was produced in the same manner as in Example 1, with the exception that the joining conditions for the sheet-shaped dried bodies were changed.

(Example 3)

[0093] As shown in Table 3, a titanium porous body was produced in the same manner as in Example 1, with the exception that three sheet-shaped dried bodies having a predetermined surface roughness Ra were used and titanium powder with an average particle diameter of 21 μm was used to produce each of them.

(Example 4)

[0094] As shown in Table 4, a titanium porous body was produced in the same manner as in Example 1, with the exception that titanium powder with an average particle diameter of 28 μm was used to produce the sheet-shaped dried body for the other-side porous layer, resulting in the sheet-shaped dried body having a predetermined surface roughness Ra, and the heating time for debinding and the sintering temperature were changed.

(Comparative Example 1)

[0095] When attempting to produce a titanium porous body in the same manner as in Example 1, with the exception that the pressure was set to zero (no pressurizing) during the joining of the sheet-shaped dried bodies, the individual porous layers of the titanium porous body peeled off easily by hand, and it was therefore not possible to produce the titanium porous body.

(Comparative Example 2)

[0096] When attempting to produce a titanium porous body in the same manner as in Example 1, with the exception that the sheet-shaped dried bodies were joined under pressure but without heating at room temperature, the sheet-shaped dried bodies failed to be joined, and subsequent steps could not be performed.

(Evaluation)

[0097] For each of the titanium porous bodies according to Examples 1 to 4, the total thickness, the thickness of each porous layer (Thickness of Each Layer), the average area of the pores opening on each of the one surface and the other surface (Average Pore Area on Surface), the standard deviation of the pore area (Standard Deviation of Pore Area on Surface), the number of pores present within a rectangular region having an area of 22,000 μm^2 and an aspect ratio of 4:3 (Number of Pores on Surface), and the overall porosity were each measured in accordance with the above methods. The results are shown in Tables 1 to 4.

[0098] In addition, the electrical conductivity (laminated) was measured for each of the one surface and the other surface of each titanium porous body. The electrical conductivity was measured using a low-resistivity meter (Loresta GP MCP-T610, manufactured by Mitsubishi Analytech Co., Ltd.) by the four-probe method, with the target surface among the above surfaces positioned upward. The probe checker used was the MCP-T610 RMH112. The results are also shown in Table 1. It is considered that if the titanium bonding surfaces of the titanium porous layers are sufficiently bonded to each other, the electrical conductivity will be high. Furthermore, when the electrical conductivity is high, each porous layer is strongly bonded, and therefore the titanium porous body is presumed to exhibit excellent mechanical strength. It should be noted that in Tables 1 to 4, the unit of electrical conductivity is represented as "E+3 S/cm", which means " $10^3 \times \text{S/cm}$ ". For example, the value "4.1" in the "Electrical Conductivity (Laminated)" column of Table 1 means 4,100 S/cm.

[0099] Tables 1 to 4 also show the thickness, electrical conductivity (single), electrical conductivity (laminated), and porosity of the titanium sintered bodies (corresponding to each porous layer) obtained by performing debinding and sintering on the sheet-shaped dried bodies used to produce each titanium porous body, without joining them together. The electrical conductivity (single) refers to the value measured separately for two or three titanium sintered bodies without laminating them, while the electrical conductivity (laminated) refers to the value measured with two or three titanium sintered bodies laminated together. Since the electrical conductivity (laminated) is measured with two or three titanium sintered bodies simply stacked on top of each other, the value tends to be lower than the electrical conductivity (single) due to the large electrical resistance between them. Furthermore, because the sheet-shaped dried bodies were laminated without being joined together, the total thickness tends not to match the sum of the individual thicknesses of the titanium sintered bodies.

[Table 1]

Example 1	Titanium Powder	Sheet-Shaped Dried Body (Porous Layer)	Dried Body Surface Roughness Ra		Joining		Debinding	Sintering	Titanium Porous Body (After Sintering)						Porosity	
	Average Particle Diameter (μm)		Resin Substrate Side (μm)	Opposite Side (μm)	Temperature (°C)	Pressure (N/cm ²)	Time (min)	Time (hr)	Temperature (°C)	Total Thickness (μm)	Thickness of Each Layer (μm)	Electrical Conductivity (Laminated) (E+3 S/cm)	Average Pore Area on Surface (μm ²)	Standard Deviation of Pore Area on Surface (μm ²)		Number of Pores on Surface (count)
	14	One Side	0.7	1.5	150	0.73	5	18	800	297	42	4	8.2	15.9	437	
	21	Other Side	0.5	2.2							255	4.1	15.2	30.0	267	

Titanium sintered body corresponding to each porous layer			
Porous Layer Position	Thickness (μm)	Electrical Conductivity (Single) (E+3 S/cm)	Electrical Conductivity (Laminated) (E+3 S/cm)
One Side	43	3.3	1.1
Other Side	259	4.1	3.6
Laminate	301		

[Table 2]

Example 2	Titanium Powder	Sheet-Shaped Dried Body (Porous Layer)	Dried Body Surface Roughness Ra		Joining		Debinding	Sintering	Titanium Porous Body (After Sintering)							Porosity
	Average Particle Diameter (μm)	Resin Substrate Side (μm)	Opposite Side (μm)	Temperature (°C)	Pressure (N/cm ²)	Time (min)	Time (hr)	Temperature (°C)	Total Thickness (μm)	Thickness of Each Layer (μm)	Electrical Conductivity (Laminated) (E+3 S/cm)	Average Pore Area on Surface (μm ²)	Standard Deviation of Pore Area on Surface (μm ²)	Number of Pores on Surface (count)		
	14	One Side	0.7	1.5	150	0.27	3	18	800	300	42	3.93	8.7	17.1	425	
	21	Other Side	0.5	2.2							258	3.9	14.5	27.4	271	

Titanium sintered body corresponding to each porous layer				
Porous Layer Position	Thickness (μm)	Electrical Conductivity (Single) (E+3 S/cm)	Electrical Conductivity (Laminated) (E+3 S/cm)	Porosity
One Side	43	3.3	1.1	45%
Other Side	259	4.1	3.6	43%
Laminate	301			

[Table 3]

Example 3	Titanium Powder	Sheet-Shaped Dried Body (Porous Layer)	Dried Body Surface Roughness Ra		Joining			Debinding	Sintering	Titanium Porous Body (After Sintering)						Porosity	
	Average Particle Diameter (μm)		Resin Substrate Side (μm)	Opposite Side (μm)	Temperature (°C)	Pressure (N/cm ²)	Time (min)	Time (hr)	Temperature (°C)	Total Thickness (μm)	Thickness of Each Layer (μm)	Electrical Conductivity (Laminated) (E+3 S/cm)	Average Pore Area on Surface (μm ²)	Standard Deviation of Pore Area on Surface (μm ²)	Number of Pores on Surface (count)		
	21	One Side	0.5	2.2						800	828	270	1.64	11.9	24.4	304	48%
	21	Intermediate	0.5	2.2	150	0.73	5	18			286	-	-	-	-	-	
	21	Other Side	0.5	2.2							272	2.57	13.2	25.9	334		

Titanium sintered body corresponding to each porous layer				
Porous Layer Position	Thickness (μm)	Electrical Conductivity (Single) (E+3 S/cm)	Electrical Conductivity (Laminated) (E+3 S/cm)	Porosity
Other Side	257	3.9	1.5	43%
Intermediate	265	-	-	44%
One Side	258	4.0	1.4	45%
Laminate	791			

[0100]

[Table 4]

Example 4	Titanium Powder	Sheet-Shaped Dried Body (Porous Layer)	Dried Body Surface Roughness Ra		Joining		Debirthing	Sintering	Titanium Porous Body (After Sintering)							Porosity
	Average Particle Diameter (μm)	Opposite Side (μm)	Resin Substrate Side (μm)	Temperature (°C)	Pressure (N/cm ²)	Time (hr)	Temperature (°C)	Total Thickness (μm)	Thickness of Each Layer (μm)	Electrical Conductivity (Laminated) (E+3 S/cm)	Average Pore Area on Surface (μm ²)	Standard Deviation of Pore Area on Surface (μm ²)	Number of Pores on Surface (count)			
	14	One Side	0.5	1.6	150	0.73	5	12	850	403	107	7.5	13.6	423		
	28	Other Side	1.5	3.2							296	25.9	68.6	191		

Titanium sintered body corresponding to each porous layer					
Porous Layer Position	Thickness (μm)	Electrical Conductivity (Single) (E+3 S/cm)	Electrical Conductivity (Laminated) (E+3 S/cm)	Porosity	
	One Side	110	4.7	1.5	39%
	Other Side	309	2.4	2.1	53%
Laminate	413				

[0101] In Examples 1 to 4, as shown in Tables 1 to 4, titanium porous bodies were successfully produced by heating sheet-shaped dried bodies at a predetermined temperature while applying a predetermined pressure. Since these

titanium porous bodies exhibit high electrical conductivity comparable to that of individual titanium sintered bodies (electrical conductivity (single)), it is recognized that the porous layers are sufficiently bonded to one another at the titanium bonding surfaces.

[0102] Furthermore, the above titanium porous bodies were laminated by bonding adjacent titanium bonding surfaces in the thickness direction, and each included multiple porous layers each having pores. For each of the titanium porous bodies, the value of the electrical conductivity (laminated) for at least one of the one-side and other-side surfaces was approximately 1.5 times or more that of the electrical conductivity (laminated) for the same surface of the simply laminated titanium sintered bodies, indicating that the porous layers are sufficiently bonded to one another. Furthermore, for each of the titanium porous bodies, the average area of the pores on one surface (the surface of the one-side porous layer), the standard deviation of the pore area, the number of pores, and the porosity all attained their respective predetermined desirable values.

[Description of Reference Numerals]

[0103]

1, 11: Mold
2, 12, 32: Resin substrate
3, 13: Sheet-shaped dried body
31: Titanium formed body
Sa1, Sb1: Surface on resin substrate side
Sa2, Sb2: Reverse surface
Ta, Tb: Thickness

Claims

1. A method for producing a sheet-shaped titanium formed body, the method comprising:
a joining step of laminating multiple sheet-shaped dried bodies, each obtained by drying a paste containing titanium powder, an organic binder, and an organic solvent, and heating the laminated bodies to a temperature of 70°C or higher and 200°C or lower while applying a pressure of 0.1 N/cm² or more in a thickness direction.
2. The method for producing a titanium formed body according to claim 1, comprising, prior to the joining step, a drying step of drying the paste to obtain sheet-shaped dried bodies.
3. The method for producing a titanium formed body according to claim 2, wherein in the drying step, the paste is heated to a temperature of 90°C or higher and 165°C or lower.
4. The method for producing a titanium formed body according to claim 2 or 3, wherein the drying of the paste in the drying step is performed on a resin substrate.
5. The method for producing a titanium formed body according to any one of claims 1 to 4, wherein in the joining step, the multiple laminated sheet-shaped dried bodies are sandwiched between molds from both sides in the thickness direction, and pressure and heating are applied.
6. The method for producing a titanium formed body according to claim 5, wherein in the joining step, pressure and heating are applied with a resin substrate interposed between the sheet-shaped dried bodies and the molds.
7. The method for producing a titanium formed body according to any one of claims 1 to 6, wherein an average particle diameter of the titanium powder in at least one of the sheet-shaped dried bodies is 10 μm or more and 20 μm or less.
8. The method for producing a titanium formed body according to any one of claims 1 to 7, wherein a difference between an average particle diameter of the titanium powder in the sheet-shaped dried body on one surface side and an average particle diameter of the titanium powder in at least one other sheet-shaped dried body is 5 μm or more.
9. The method for producing a titanium formed body according to any one of claims 1 to 8, wherein the paste used to

produce the sheet-shaped dried bodies does not comprise a foaming agent.

10. A method for producing a sheet-shaped titanium porous body, the method comprising:

a debinding step of heating a titanium formed body produced by the method for producing a titanium formed body according to any one of claims 1 to 9 to volatilize the organic binder in the titanium formed body; and a sintering step of heating the titanium formed body after the debinding step to sinter the titanium powder in the titanium formed body.

11. A sheet-shaped titanium porous body, comprising

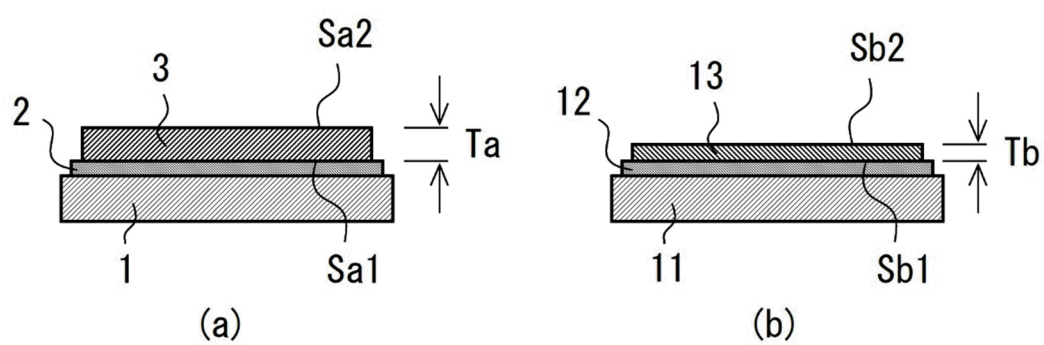
multiple titanium porous layers, each having pores through which a gas and/or a liquid can pass, wherein adjacent titanium bonding surfaces in a thickness direction are bonded and laminated to one another, and wherein an average area of pores opening on a surface of the porous layer that forms one surface of the multiple porous layers is $5\ \mu\text{m}^2$ or more and $15\ \mu\text{m}^2$ or less, a standard deviation of areas of the pores is $35\ \mu\text{m}^2$ or less, and a number of the pores present within a rectangular region having an area of $22,000\ \mu\text{m}^2$ and an aspect ratio of 4:3 is 256 or more, and the overall porosity including the multiple porous layers is 40% or more and 60% or less.

12. The titanium porous body according to claim 11, wherein an average area of pores opening on other surface located on a reverse side of the one surface is 1.5 times or more the average area of the pores opening on the one surface.

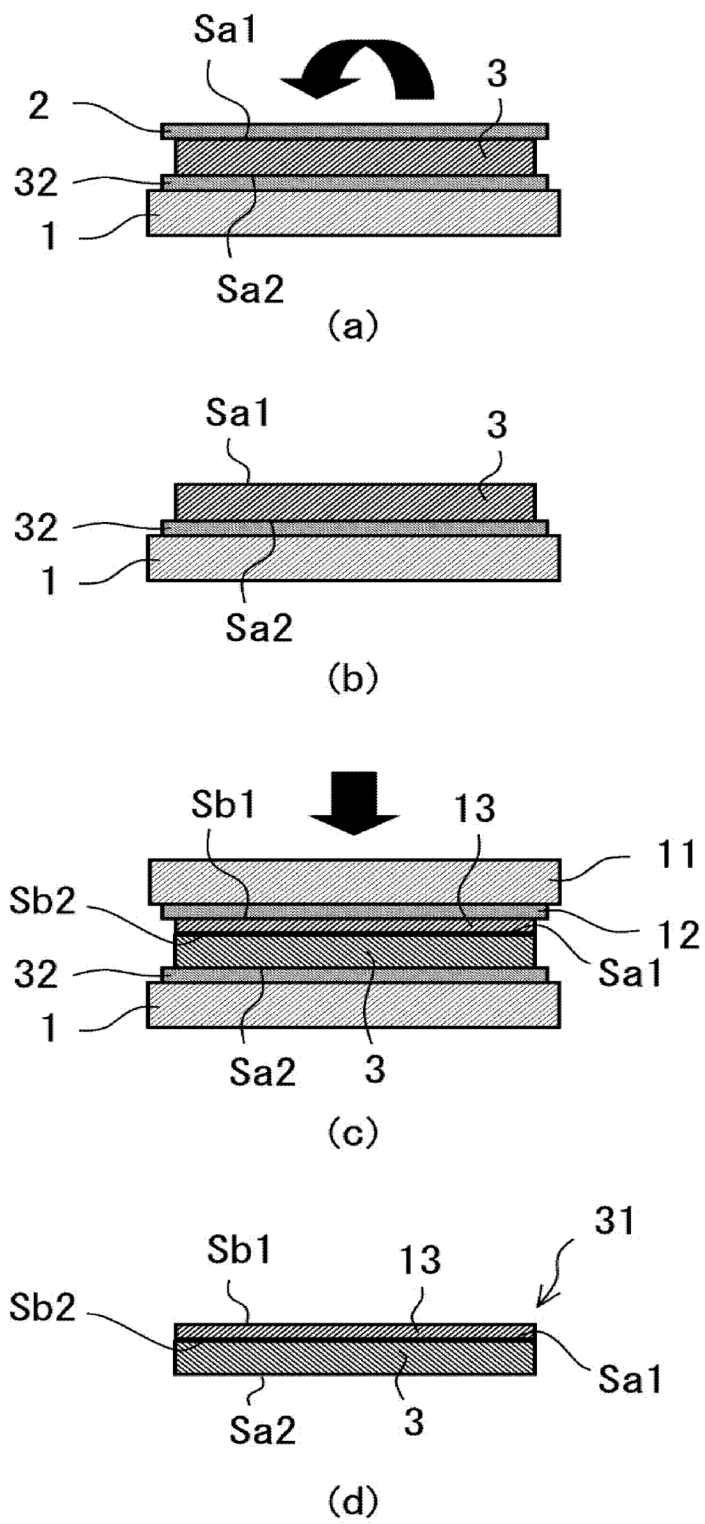
13. The titanium porous body according to claim 11 or 12, wherein the total thickness is $200\ \mu\text{m}$ or more and $3,000\ \mu\text{m}$ or less.

14. The titanium porous body according to any one of claims 11 to 13, wherein a thickness of the porous layer forming a portion on the one surface side is 30% or less of the total thickness.

[Fig. 1]



[Fig. 2]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/031074

A. CLASSIFICATION OF SUBJECT MATTER

B22F 7/06(2006.01)i; **B22F 1/00**(2022.01)i; **B22F 3/00**(2021.01)i; **B22F 3/02**(2006.01)i; **B22F 3/11**(2006.01)i;
C22C 1/08(2006.01)i; **C25B 11/031**(2021.01)i

FI: B22F7/06 D; B22F1/00 R; C22C1/08 C; B22F3/02 G; C25B11/031; B22F3/00 A; B22F3/11 B

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)

B22F7/00-7/08; B22F3/00-3/24; H01M8/00-8/2495; C25B9/00-9/77; C22C1/08; C25B11/03-11/037; B32B15/00-15/20

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 1971-2024
 Registered utility model specifications of Japan 1996-2024
 Published registered utility model applications of Japan 1994-2024

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004-68112 A (SUMITOMO TITANIUM CORP.) 04 March 2004 (2004-03-04) claims, paragraphs [0001]-[0048], fig. 1-4	1-14
X	WO 2022/210681 A1 (MITSUBISHI MATERIALS CORPORATION) 06 October 2022 (2022-10-06) claims, examples, fig. 1, 3	11-14
A	JP 2014-84505 A (TOHO TITANIUM CO., LTD.) 12 May 2014 (2014-05-12) examples	4
A	WO 2019/188480 A1 (TOHO TITANIUM CO., LTD.) 03 October 2019 (2019-10-03) entire text	11-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

25 October 2024

Date of mailing of the international search report

12 November 2024

Name and mailing address of the ISA/JP

**Japan Patent Office (ISA/JP)
 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915
 Japan**

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/031074

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The only feature shared with the invention in claims 1-14 is a titanium laminate. The invention in claims 1-9 does not specify a porous body, manufacture of a porous body, or the like, and is therefore not the manufacturing method of the invention in claims 11-14. Moreover, although claim 10 specifies manufacture of a porous body, this porous body is not limited to having the holes and the porosity of the porous layer of claims 11-14, and therefore the invention in claim 10 is not the manufacturing method of the invention in claims 11-14. A titanium multilayer porous body was disclosed in JP 2004-68112 A and WO 2022/210681 A1 prior to the priority date of the present application, and is therefore not a special technical feature. Accordingly, the following two inventions are acknowledged.

(Invention 1)

The invention in claims 1-10 is a method for manufacturing a titanium molded body using a specific sheet-form titanium molded body, or a method for manufacturing a titanium porous body.

(Invention 2)

The invention in claims 11-14 is a titanium porous body including a plurality of porous layers and having specific holes and a specific porosity.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2024/031074

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP	2004-68112	A	04 March 2004	(Family: none)	
WO	2022/210681	A1	06 October 2022	JP 2022-151916	A
claims, examples, fig. 1, 3					
JP	2014-84505	A	12 May 2014	(Family: none)	
WO	2019/188480	A1	03 October 2019	US 2021/0016352	A1
				entire text	
				EP 3778074	A1
				CN 111886091	A
				KR 10-2020-0134235	A

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- JP 2011106023 A [0006]
- JP 2021529891 A [0006]