



(11) **EP 4 332 273 A1**

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

(43) Date of publication:
06.03.2024 Bulletin 2024/10

(51) International Patent Classification (IPC):
C25C 3/28 (2006.01) C22B 34/12 (2006.01)

(21) Application number: **22795326.2**

(52) Cooperative Patent Classification (CPC):
C22B 34/12; C25C 3/28

(22) Date of filing: **14.03.2022**

(86) International application number:
PCT/JP2022/011426

(87) International publication number:
WO 2022/230403 (03.11.2022 Gazette 2022/44)

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

(30) Priority: **30.04.2021 JP 2021077965**

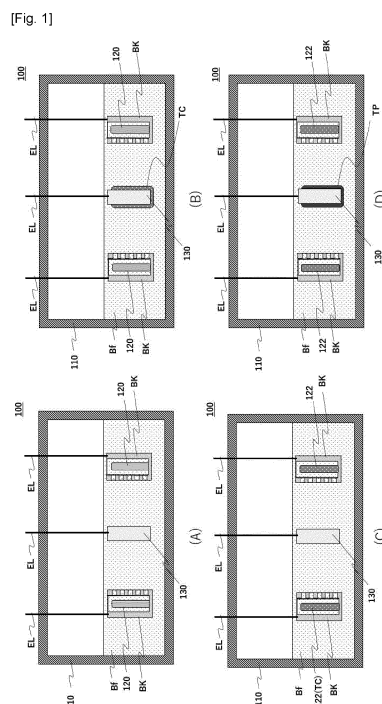
(71) Applicant: **Toho Titanium CO., LTD.**
Chigasaki-shi
Kanagawa 253-8510 (JP)

(72) Inventors:
• **SUZUKI, Daisuke**
Chigasaki-shi, Kanagawa 253-8510 (JP)
• **NAKAJO, Yuta**
Chigasaki-shi, Kanagawa 253-8510 (JP)
• **KUMAMOTO, Kazuhiro**
Chigasaki-shi, Kanagawa 253-8510 (JP)
• **HORIKAWA, Matsuhide**
Chigasaki-shi, Kanagawa 253-8510 (JP)
• **FUJII, Hideki**
Chigasaki-shi, Kanagawa 253-8510 (JP)

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

(54) **METAL TITANIUM PRODUCTION METHOD AND METAL TITANIUM ELECTRODEPOSIT**

(57) Provided is a method for producing metal titanium by molten salt electrolysis using a conductive material containing titanium, aluminum, oxygen and other impurities. A method for producing metal titanium, wherein a refining process includes: a rough electrodeposition step of performing a molten salt electrolysis using an electrode containing a TiAlO conductive material in a chloride bath Bf to obtain a titanium-containing electrodeposit TC; and one or more refinement electrodeposition steps of performing a molten salt electrolysis using an electrode containing the titanium-containing electrodeposit TC in a chloride bath Bf, and wherein at least one of the chloride bath Bf used for the rough electrodeposition step and the chloride bath Bf used for the refinement electrodeposition step contains 30 mol % or more of magnesium chloride.



Description

[Technical Field]

5 **[0001]** The present invention relates to a metal titanium production method and a metal titanium electrodeposit.

[Background Art]

10 **[0002]** In general, production of metal titanium is carried out by a Kroll process. However, the production involves many processes.

[0003] By the way, techniques of mainly producing a titanium alloy by molten salt electrolysis are conventionally known in the art. For example, Patent Literature 1 discloses a method for producing a titanium alloy by heating a raw material containing titanium ore and aluminum and then subjecting the obtained material to molten salt electrolysis.

15 [Citation List]

[Patent Literature]

20 **[0004]** [PTL 1]
Japanese Patent Application Publication No. 2015-507696 A

[Summary of Invention]

[Technical Problem]

25 **[0005]** In the production method described in Patent Literature 1, a chloride bath containing of sodium chloride and potassium chloride is used to refine the titanium alloy. In the refining, a refined titanium product having a predetermined aluminum content and oxygen content is obtained (see Table 3 of Patent Literature 1). Such refined titanium product has at least a high aluminum content, resulting in a raw material for aluminum-containing titanium alloy products. However,
30 it is not suitable for the production of other titanium alloy products and titanium metal products.

[0006] Thus, in an embodiment, an object of the present invention is to provide a method for producing metal titanium by molten salt electrolysis using a conductive material containing titanium, aluminum, oxygen and other impurities.

[Solution to Problem]

35 **[0007]** The present inventors have conducted various studies in order to reduce contents of impurities (particularly, the content of oxygen) by molten salt electrolysis to obtain a titanium alloy as in the invention disclosed in Patent Literature 1, for example, and found that not only the content of oxygen but also the content of aluminum can be surprisingly reduced depending on the composition of the chloride bath used during the molten salt electrolysis.

40 **[0008]** For example, the molten salt electrolysis may be performed for the purpose of refining metals and alloys. As a result of intensive studies on how to reduce the oxygen content while maintaining the composition of the titanium base alloy, the present inventors have found that when the molten salt electrolysis is performed using a chloride bath containing a predetermined amount of magnesium chloride, not only contents of impurities other than oxygen and aluminum but also the content of aluminum can be reduced. On the other hand, when the molten salt electrolysis is carried out in a
45 chloride bath containing sodium chloride and potassium chloride as in the production method described in Patent Literature 1, the aluminum content cannot be sufficiently reduced.

[0009] This enables metal titanium to be produced from titanium ore without carrying out the Kroll method, for example. The use of the metal titanium also allows titanium alloy products that do not contain aluminum to be produced.

50 **[0010]** Thus, in an aspect, the present invention provides a method for producing metal titanium, comprising: a refining process of refining a TiAlO conductive material containing titanium, aluminum, and oxygen, wherein the refining process comprises a rough electrodeposition step of performing a molten salt electrolysis using an electrode containing the TiAlO conductive material in a chloride bath to obtain a titanium-containing electrodeposit; and after the rough electrodeposition step, one or more refinement electrodeposition steps of performing a molten salt electrolysis using an electrode containing the titanium-containing electrodeposit in a chloride bath, and

55 wherein at least one of the chloride bath used for the rough electrodeposition step and the chloride bath used for the refinement electrodeposition step contains 30 mol % or more of magnesium chloride.

[0011] In an embodiment of the method for producing metal titanium according to the present invention, at least one of the chloride bath used for the rough electrodeposition step and the chloride bath used for the refinement electrodepo-

sition step contains 50 mol % or more of magnesium chloride.

[0012] In an embodiment of the method for producing metal titanium according to the present invention, each of the chloride bath used for the rough electrodeposition step and at least one chloride bath used for the refinement electrodeposition steps contains 30 mol % or more of magnesium chloride.

[0013] In an embodiment of the method for producing metal titanium according to the present invention, each of the chloride bath used for the rough electrodeposition step and at least one chloride bath used for the refinement electrodeposition steps contains 50 mol % or more of magnesium chloride.

[0014] In an embodiment of the method for producing metal titanium according to the present invention, further comprising an extracting process of heating a chemical blend comprising a titanium ore containing titanium oxide, aluminum, and a separating agent to obtain the TiAlO conductive material, before the refining process.

[0015] In an embodiment of the method for producing metal titanium according to the present invention, a molar ratio of the titanium oxide, the aluminum and the separating agent contained in the chemical blend is 3:4-7:2-6.

[0016] In an embodiment of the method for producing metal titanium according to the present invention, the separating agent comprises one or more selected from calcium fluoride, calcium oxide and sodium fluoride.

[0017] In an embodiment of the method for producing metal titanium according to the present invention, the metal titanium has an aluminum content of 100 ppm by mass or less and an oxygen content of 500 ppm by mass or less.

[0018] In an embodiment of the method for producing metal titanium according to the present invention, the metal titanium has a nitrogen content of 0.03% by mass or less, a carbon content of 0.01 % by mass or less, an iron content of 0.010% by mass or less, a magnesium content of 0.05% by mass or less, a nickel content of 0.01 % by mass or less, a chromium content of 0.005% by mass or less, a silicon content of 0.001% by mass or less, a manganese content of 0.05% by mass or less, and a tin content of 0.01 % by mass or less.

[0019] Also, in another aspect, the present invention provides a metal titanium electrodeposit, wherein the metal titanium electrodeposit has an aluminum content of 5 ppm by mass or more and 100 ppm by mass or less, and an oxygen content of 100 ppm by mass or more and 500 ppm by mass or less.

[0020] In an embodiment of the metal titanium electrodeposit according to the present invention, the metal titanium electrodeposit has a nitrogen content of 0.001% by mass or more and 0.03% by mass or less, a carbon content of 0.0004% by mass or more and 0.01% by mass or less, an iron content of 0.010% by mass or less, a magnesium content of 0.05% by mass or less, a nickel content of 0.01% by mass or less, a chromium content of 0.005% by mass or less, a silicon content of 0.001% by mass or less, a manganese content of 0.05% by mass or less, and a tin content of 0.01 % by mass or less.

[Advantageous Effects of Invention]

[0021] According to an embodiment of the present invention, it is possible to provide a method for producing metal titanium by molten salt electrolysis using a conductive material containing titanium, aluminum, and oxygen.

[Brief Description of Drawings]

[0022]

[Fig. 1]

Figs. 1(A) to (D) are diagrams for explaining a refining process in an embodiment of a method for producing metal titanium according to the present invention.

[Fig. 2]

Figs. 2(A) to (D) are diagrams for explaining a refining process in another embodiment of a method for producing metal titanium according to the present invention.

[Fig. 3]

Figs. 3(A) to (D) are diagrams for explaining a refining process in another embodiment of a method for producing metal titanium according to the present invention.

[Fig. 4]

Figs. 4(A) to (D) are diagrams for explaining a refining process in another embodiment of a method for producing metal titanium according to the present invention.

[Fig. 5]

Figs. 5(A) to (D) are diagrams for explaining a refining process in another embodiment of a method for producing metal titanium according to the present invention.

[Fig. 6]

Figs. 6(A) to (D) are diagrams for explaining a refining process in Example 1.

[Fig. 7]

Fig. 7 is a diagram taken along the line X-X of Fig. 6(A).

[Fig. 8]

Fig. 8(A) is a photograph of a titanium-containing electrodeposit after a rough electrodeposition step obtained in Example 1, and Fig. 8(B) is a photograph obtained by SEM observation of a titanium-containing electrodeposit after the rough electrodeposition step obtained in Example 1.

[Fig. 9]

Fig. 9 (A) is a photograph of a metal titanium electrodeposit after a refinement electrodeposition step obtained in Example 1, and Fig. 9(B) is a photograph obtained by SEM observation of a metal titanium electrodeposit after the refinement electrodeposition step obtained in Example 1.

[Description of Embodiments]

[0023] The present invention is not limited to embodiments described below, and it can be embodied by modifying components without departing from the spirit of the present invention. Moreover, various inventions can be formed by appropriately combining a plurality of components disclosed in each embodiment. For example, the invention may be formed by omitting some components from all the components shown in the embodiments. In addition, in the drawings, some members are schematically shown in order to facilitate understanding of the embodiments included in the invention, and illustrated sizes, positional relationships, and the like, may not necessarily be accurate.

[0024] As used herein, the "metal titanium electrodeposit" is generally granular when the appearance is visually observed, and it often has a three-dimensional shape in which dendritic or polyhedral fine grains are linked, when microscopically observed (Fig. 9(B)).

[1. Method for Producing Metal Titanium]

[0025] In an embodiment, a method for producing metal titanium according to the present invention includes a refining process for reducing an impurity content. It should be noted that an extraction process may be further included before the refining process.

[0026] An example of each step is described below.

<Extraction Process >

[0027] In the extraction process, for example, a chemical blend containing titanium ore containing titanium oxide, aluminum, and a separating agent are heated to obtain a TiAlO conductive material. The following reactions would be utilized by the heating. That is, in the extraction process, a thermite reaction is used to reduce titanium oxide, which is a metal oxide, with aluminum. The chemical blend is a raw material mixture for obtaining a TiAlO conductive material. Titanium oxide in the titanium ore is not suitable for molten salt electrolysis due to its low electrical conductivity. Therefore, the TiAlO conductive material can be produced by performing the extraction process using the titanium ore. Since the TiAlO conductive material has a relatively high electrical conductivity, it can be used in a refining process for producing metal titanium, which will be described below. In the extraction process, the TiAlO conductive material may be produced by appropriately referring to the known method described in Patent Literature 1 (Japanese Patent Application Publication No. 2015-507696) or the like.

(Titanium Ore)

[0028] Although the content of titanium oxide in the titanium ore is not limited, it is, for example, 50% by mass or more, for example, 80% by mass or more, and for example, 90% by mass or more. The titanium ore includes ore that has been obtained by mining, as well as ore that has been so-called upgraded. When the content of titanium oxide in the titanium ore is lower, an appropriate treatment such as leaching may be carried out to improve (i.e., upgrade) the content of titanium oxide.

(Separating Agent)

[0029] The separating agent is mixed into the chemical blend for the purpose of separating the TiAlO conductive material from a slag as a by-product, in the extraction process. An agent having such a function can be used as a separating agent, and it preferably contains one or more selected from calcium fluoride, calcium oxide and sodium fluoride. From the viewpoint of morphology in the reaction during the heating, the separating agent more preferably contains calcium fluoride. Therefore, the separating agent may be calcium fluoride alone.

(Chemical Blend Composition)

[0030] In order to produce the above chemical blend, amounts of titanium ore, aluminum and separating agent introduced are adjusted so that a molar ratio of titanium oxide: aluminum: separating agent = 3:4-7:2-6, for example. Thus, the molar ratio of titanium oxide, aluminum and separating agent in the chemical blend is 3:4-7:2-6.

(Heating Conditions)

[0031] For the heating conditions, a temperature inside a container is, for example, 1500°C or more and 1800°C or less in an inert gas (e.g., Ar) atmosphere. Examples of a material for an inner wall of the container include carbon, ceramics, and the like, in terms of heat resistance and the like.

(TiAlO Conductive Material)

[0032] The TiAlO conductive material obtained in the extraction process has, for example, a titanium content of 50% by mass or more and 80% by mass or less, an aluminum content of 3% by mass or more and 40% by mass or less, and an oxygen content of 0.2% by mass or more and 40% by mass or less.

[0033] The lower limit of the titanium content is, for example, 60% by mass or more.

[0034] Also, the lower limit of the aluminum content is, for example, 5% by mass or more. On the other hand, the upper limit of the aluminum content is, for example, 30% by mass or less, for example, 20% by mass or less.

[0035] Also, the lower limit of the oxygen content is, for example, 3% by mass or more, 5% by mass or more, or 8% by mass or more. On the other hand, the upper limit of the oxygen content is, for example, 30% by mass or less, for example, 20% by mass or less.

[0036] In the present invention, a TiAlO conductive material having such high aluminum and oxygen contents can also provide metal titanium with a low impurity content and high purity.

[0037] In addition, as for the method for measuring the impurity content of each component of the TiAlO conductive material, the measuring method described in Examples of this specification can be used.

(Specific Resistance)

[0038] The upper limit of the specific resistance of the TiAlO conductive material may be, for example, $1 \times 10^{-4} \Omega \cdot m$ or less, in terms of efficiently performing molten salt electrolysis in the refining process described below for producing the metal titanium. Also, the lower limit of the specific resistance may be, for example, $1 \times 10^{-8} \Omega \cdot m$ or more, because the TiAlO conductive material may be moderately conductive. The lower limit of the specific resistance may be, for example, $1 \times 10^{-7} \Omega \cdot m$ or more, for example, $5 \times 10^{-7} \Omega \cdot m$ or more.

[0039] With regard to the method for measuring the resistivity of the TiAlO conductive material, the measuring method described in Examples of this specification can be used.

<Refining Process>

[0040] In the refining process, an electrolytic device is used to refine the TiAlO conductive material in order to reduce the impurity content. That is, in the refining process, the metal titanium with a high purity is obtained by reducing the contents of mainly aluminum and oxygen in the TiAlO conductive material, as well as contents of other ore-derived elements. The refining process includes a rough electrodeposition step and one or more refinement electrodeposition steps of performing molten salt electrolysis using an electrode containing the titanium-containing electrodeposit obtained in the rough electrodeposition step.

(Electrolytic Device)

[0041] In an embodiment, various electrolytic devices can be used. An example of an electrolysis device 100 shown in Fig. 1(A) is of a batch type, and includes a device including: an electrolytic bath 110 in a form of a sealed container that stores a chloride bath Bf; an electrode including anodes 120 and a cathode 130 that are immersed and arranged in the chloride bath Bf; and a power source (not shown) connected to the anodes 120 and the cathode 130 via electrically conductive lines to conduct current through the anodes 120 and the cathode 130. Although not shown, the electrolytic device 100 typically has a structure that can be opened and closed in order to install or take out the anode and the cathode. Although not shown, the electrolytic device 100 has an opening for feeding or discharging a gas in order to make the space above the chloride bath Bf an inert gas atmosphere. Although not shown, the electrolytic device 100 is provided with a heater at an appropriate position, so that the chloride bath Bf can be maintained in a molten state by

heating. The material of the electrolytic bath 110 is not particularly limited as long as it has heat resistance and corrosion resistance. Also, the electrodes may further include a bipolar electrode.

(Molten Salt)

[0042] The molten salt that forms the chloride bath may contain, for example, 70 mol% or more, for example, 80 mol% or more, for example, 90 mol% or more, of an alkali metal chloride and an alkaline earth metal chloride. In the present invention, the reasons that not use a fluoride bath, a bromide bath and an iodide bath in place of the chloride bath include high corrosiveness, high environmental load and high cost.

[0043] At least one chloride bath Bf of the chloride bath used for the rough electrodeposition step and the chloride bath used for the refinement electrodeposition step contains 30% by mass or more of magnesium chloride, in view of reducing not only the oxygen content but also the aluminum content to produce metal titanium. The use of the chloride bath having a high magnesium chloride content can increase the effect of reducing the aluminum content. It should be noted that, for example, only the chloride bath used for the rough electrodeposition step may contain a predetermined amount of magnesium chloride, or only at least one chloride bath of the chloride baths used in one or more refinement electrodeposition steps may contain the predetermined amount of magnesium chloride. In addition, at least one of the chloride bath used for the rough electrodeposition step and the chloride baths used in the one or more refinement electrodeposition steps may contain the predetermined amount of magnesium chloride.

[0044] Also, from the viewpoint of more reliably reducing the aluminum content and oxygen content of the electrodeposit, each of the chloride bath used for the rough electrodeposition step and at least one chloride bath used in the one or more refinement steps may contain the predetermined amount of magnesium chloride described above.

[0045] The above chloride bath containing the predetermined amount of magnesium chloride is effective for reducing the aluminum content and oxygen content in the electrodeposit, and the lower limit of the magnesium chloride content is preferably 30 mol % or more, and more preferably 50 mol % or more, and still more preferably 80 mol % or more, and even more preferably 85 mol % or more, and still more preferably 90 mol % or more. The chloride bath contains, for example, 70 mol% or less, 50 mol% or less, 20 mol% or less, 15 mol% or less, or 10 mol % or less, of at least one metal chloride selected from lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), rubidium chloride (RbCl), cesium chloride (CsCl), beryllium chloride (BeCl₂), calcium chloride (CaCl₂), strontium chloride (SrCl₂), and barium chloride (BaCl₂). Further, the chloride bath may optionally contain a lower titanium chloride, including, for example, titanium dichloride and titanium trichloride. The content of the lower titanium chloride may be appropriately adjusted.

[0046] For the above chlorides, the specific type and content of salts can be determined as appropriate in view of an operating temperature and the like. The content on a molar basis is measured by ICP emission spectrometry and atomic absorption spectrometry.

[0047] Here, the above content on the molar basis is calculated as follows. After solidifying a molten salt sample collected from the chloride bath, the components of the sample are subjected to ICP emission spectrometry and atomic absorption spectrometry to calculate the content of each metal ion on a molar basis in the chloride bath Bf. If the chloride bath contains MgCl₂, NaCl, KCl, CaCl₂, LiCl, TiCl₂ and TiCl₃, the total metal ion content (Mm) is determined by adding up the content of magnesium ions, the content of sodium ions, the content of potassium ions, the content of calcium ions, the content of lithium ions, and the content of titanium ions, by the atomic absorption spectrometry for Na and K, and by ICP emission spectrometry for the other elements. The content on the molar basis for each component contained in the chloride bath can be calculated by dividing the metal ion content of each component by the total metal ion content (Mm), and expressing it as a percentage. As described above, the content of the chloride is determined based on the contents of the metal ions contained in the chloride bath.

(Anode and Cathode)

[0048] Each of the anode 120 and the cathode 130 can have, for example, a rod shape, a long band that is used while being moved, a cylindrical shape, a plate shape, a columnar shape or other pillar shapes, or a block shape. For example, the TiAlO conductive material as the anode 120 can be melted and cast to form the anode. If the distance between the electrodes of the anode 120 and the cathode 130 is to be set within a specific range, it is preferable that the shapes of the opposing portions of the anode 120 and the cathode 130 are analogous in a vertical cross section. For example, if a cylindrical, rod shaped, or pillar shaped cathode 130 is used and the anode 120 is placed outside it, the anode 120 may also be cylindrical. In this case, the cylindrical anode 120 surrounds the cathode 130, so that the area where the electrodeposits are produced can be increased. Alternatively, a rod shaped or pillar shaped cathode 130 that is rotatable with a fixed axial position may be used, and a plate shaped anode 120 having an arc shaped cross section may be used at the opposed portion. Even in this case, the opposing portions of the anode 120 and the cathode 130 can maintain substantially the same distance between the electrodes.

[0049] Alternatively, the anode 120 may be formed by placing the TiAlO conductive material obtained in the above

extraction step in the form of granules or powder in a metal basket (for example, a nickel basket) having a lower ionization tendency than that of titanium. In this case, the basket BK has many through holes, and the shape of the basket BK can be regarded as the shape of the anode 120. Further, even if current conduction is intended for the basket, the basket BK is difficult to be eluted into the chloride bath Bf, and the TiAlO conductive material is mainly eluted. In the description using the drawings, for ease of understanding, the portion where the TiAlO conductive material or the like is eluted is

[0050] Also, as for the shape of the cathode 130, at least a part of the surface of the cathode 130 on which the metal titanium is deposited may be curved. The use of such a cathode 130 allows the metal titanium to be electrodeposited on the surface of the cathode 130 while rotating the cathode 130, which contributes to miniaturization of the device during continuous production.

[0051] Next, examples of the rough electrodeposition step and the refinement electrodeposition step will be described with reference to Figs. 1(A) to (D) through Figs. 5(A) to (D).

[0052] It should be noted that when the chloride bath used for the rough electrodeposition step has a bath composition containing the above predetermined amount of magnesium chloride, the chloride bath used for the refinement electrodeposition step may have a bath composition containing the above predetermined amount of magnesium chloride, or may be another bath composition that does not contain the above predetermined amount of magnesium chloride. Further, when the chloride bath used for the refinement electrodeposition step has the bath composition containing the predetermined amount of magnesium chloride as described above, the chloride bath used for the rough electrodeposition step may have a bath composition containing the above predetermined amount of magnesium chloride, or may be another bath composition that does not contain the above predetermined amount of magnesium chloride.

[0053] Also, each of electrically conductive lines shown in Figs. 1(A) to (D) through Figs. 5(A) to 5(D) can be connected to a power supply (not shown), and a control mechanism (not shown) for the power supply is capable of appropriately switching the electrically conductive lines for supplying current according to each anode and each cathode.

<Rough Electrodeposition Step>

[0054] In the rough electrodeposition step, a titanium-containing electrodeposit is obtained by performing molten salt electrolysis using an electrode containing a TiAlO conductive material in a chloride bath Bf.

[0055] For example, in the rough electrodeposition step, as shown in Fig. 1(A), nickel baskets BK each having the TiAlO conductive material as the anode 120 and a titanium cathode 130 are arranged in the chloride bath Bf. The control mechanism then supplies current to the anodes 120 and the cathode 130 via electrically conductive lines EL connected to the baskets BK and the cathode 130, thereby performing the molten salt electrolysis.

[0056] Although the anodes 120 are placed in separate baskets BK in the drawings, the anodes may be placed in, for example, ring shaped nickel baskets (see Figs. 6(A) and 7). Alternatively, a rod shaped or plate shaped anode obtained by casting the TiAlO conductive material may be directly connected to the electrically conductive line without using the basket.

(Temperature and Current Density of Chloride Bath)

[0057] The temperature of the chloride bath Bf may be changed as needed depending on the components in the chloride bath Bf. That is, the temperature of the chloride bath Bf may be appropriately determined from the viewpoints of maintaining the molten state of the chloride bath, eliminating energy loss due to excessive heating, and the like. In this case, it is also possible to appropriately determine the temperature of the chloride bath Bf with reference to the melting point of each metal chloride. To give a specific example, the temperature of the chloride bath Bf is controlled within a range of, for example, 450°C or more and 900°C or less.

[0058] Also, the current density of the cathode 130 is not particularly limited and it may be determined as needed. The current density of the cathode 130 may be, for example, higher than or equal to 0.01 A/cm² and less than or equal to 5 A/cm². The current density of the cathode 130 can be calculated by the equation: current density (A/cm²) = current (A) / electrolytic area (cm²). Here, for example, in the case of a cathode having a cylindrical surface, the electrolytic area is calculated by the equation: electrolytic area (cm²) = cathode immersion surface area = cathode diameter (cm) × π × cathode height (cm).

[0059] In addition to continuous flowing of the current through the electrode, a pulse current may be used in which a current conduction stop period for setting the current value to zero (that is, no current conduction), and the current conduction period and the current conduction stop period are alternately repeated.

[0060] The interior of the electrolytic bath 110 is controlled to an inert atmosphere, such as argon, from the viewpoint of suppressing an increase in the contents of impurities in the titanium-containing electrodeposit due to contamination of moisture in the atmosphere.

[0061] Next, as shown in Fig. 1(B), the anodes 120 are consumed as the anodes 120 containing titanium that has a

higher ionization tendency than nickel is eluted into the chloride bath Bf to form a titanium-containing electrodeposit TC having a reduced impurity content on the surface of the cathode 130. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0062] The titanium-containing electrodeposit TC formed on the surface of the cathode 130 taken out from the electrolytic bath 110 is recovered by peeling it with a cutting tool or the like. The titanium-containing electrodeposit TC may be washed and dried as described below. The washing and drying may be performed together with the cathode 130 or may be performed after recovery from the cathode 130.

[0063] As an example, the cathode 130 is removed from the electrolytic bath 110, and the cathode 130 and the titanium-containing electrodeposit TC are washed with an acid and/or water to dissolve and remove the molten salt adhering thereto. The titanium-containing electrodeposit TC is peeled off from the surface of the cathode 130 with a cutting tool or the like. The titanium-containing electrodeposit TC is then placed in a container and vacuum-dried to evaporate moisture.

<Refinement Electrodeposition Step>

[0064] After the rough electrodeposition step, the refinement electrodeposition step is performed by carrying out molten salt electrolysis in a chloride bath Bf using an electrode containing the titanium-containing electrodeposit TC. Thus, the titanium-containing electrodeposit TC obtained in the rough electrodeposition step can be further refined to provide a metal titanium electrodeposit TP having a further reduced impurity content. One or more refinement electrodeposition steps can be performed, and after the second refinement electrodeposition step, the metal titanium electrodeposit obtained in the previous step is used as an electrode.

[0065] For example, as shown in Fig. 1(C), nickel baskets BK each having the titanium-containing electrodeposit TC as the anode 122 and a titanium cathode 130 are arranged in a chloride bath Bf. The control mechanism supplies current to the anodes 122 and the cathode 130 via electrically conductive lines EL connected to the baskets BK and the cathode 130, thereby performing the molten salt electrolysis. The cathode 130 may be the same as the cathode 130 used in the rough electrodeposition step, or may be replaced with a new cathode.

[0066] The composition of the chloride bath Bf, the temperature and the current density of the chloride bath, in the refinement electrodeposition steps, are the same as those in the rough electrodeposition steps, so the descriptions are omitted.

[0067] Next, as shown in Fig. 1(D), the titanium-containing anodes 122 are consumed as they are eluted into the chloride bath Bf to form a metal titanium electrode deposit TP having a reduced impurity content on the surface of the cathode 130. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0068] The metal titanium electrodeposit TP formed on the surface of the cathode 130 taken out from the electrolytic bath 110 is recovered by peeling it with a cutting tool or the like. The titanium metal electrodeposit TP may be subjected to the washing and drying described above in the rough electrodeposition step. The washing and drying may be performed together with the cathode 130 or may be performed after recovery from the cathode 130.

[0069] This results in titanium metal with reduced aluminum and oxygen contents.

[0070] In the embodiment shown in Figs. 1(C) to (D), the refinement electrodeposition step is performed once, but in order to further reduce the impurity content and further improve the purity of metal titanium, multiple refinement electrodeposition steps may be performed. More particularly, the resulting metal titanium electrodeposit TP is placed in a nickel basket BK in the electrolytic bath 110, and the control mechanism supplies current between the metal titanium electrodeposit TP as the anode and the titanium cathode 130, thereby performing the molten salt electrolysis. Every time such an operation is repeated, it becomes possible to recover metal titanium in which the aluminum content and the oxygen content are more reliably reduced. However, from the viewpoint of production costs, the number of repetitions may be appropriately selected. For example, one or more and five or less, for example, one or more and three or less refinement electrodeposition steps are carried out.

(Composition of Metal Titanium)

[0071] According to the above refining process, it is possible to obtain metal titanium having a controlled composition containing an aluminum content of 100 ppm by mass or less, an oxygen content of 500 ppm by mass or less, the balance being titanium and unavoidable impurities. These unavoidable impurities are often ore-derived impurities and chloride bath-derived components. The composition of metal titanium as used herein corresponds to the titanium purity of so-called Commercially Pure titanium, and the metal titanium has a low impurity content, for example, the total impurity content is 3000 ppm by mass or less.

[0072] The upper limit of the aluminum content is, for example, 50 ppm by mass or less. On the other hand, the lower limit of the aluminum content is, for example, 10 ppm by mass or more, for example 20 ppm by mass or more.

[0073] Also, the upper limit of the oxygen content is, for example, 450 ppm by mass or less, for example, 400 ppm by

mass or less. On the other hand, the lower limit of the oxygen content is, for example, 100 ppm by mass or more, for example 200 ppm by mass or more.

[0074] Further, in a further embodiment, when the above unavoidable impurities and the like are more specifically identified, it is also possible to obtain metal titanium having a further controlled composition of a nitrogen content of 0.03% by mass or less, a carbon content of 0.01 % by mass or less, an iron content of 0.010% by mass or less, a magnesium content of 0.05% by mass or less, a nickel content of 0.01 % by mass or less, a chromium content of 0.005% by mass or less, a silicon content of 0.001% by mass or less, a manganese content of 0.05% by mass or less and a tin content of 0.01 % by mass or less.

[0075] The lower limit of the nitrogen content is, for example, 0.002% by mass or more, for example 0.003% by mass or more. On the other hand, the upper limit of the nitrogen content is, for example, 0.009% by mass or less, for example, 0.008% by mass or less.

[0076] The lower limit of the carbon content is, for example, 0.0006% by mass or more, for example 0.0008% by mass or more. On the other hand, the upper limit of the carbon content is, for example, 0.008% by mass or less, for example, 0.004% by mass or less.

[0077] Also, the upper limit of the iron content is, for example, 0.005% by mass or less, for example, 0.003% by mass or less. On the other hand, the lower limit of the magnesium content is, for example, 0.001% by mass or more, for example 0.005% by mass or more.

[0078] The upper limit of the nickel content is, for example, 0.008% by mass or less, for example, 0.004% by mass or less.

[0079] The lower limit of the chromium content is, for example, 0.0005% by mass or more, for example 0.001% by mass or more.

[0080] The upper limit of the silicon content is, for example, 0.0005% by mass or less.

[0081] In addition, the lower limit of the manganese content is, for example, 0.001% by mass or more, for example, 0.005% by mass or more. On the other hand, the upper limit of the manganese content is, for example, 0.03% by mass or less.

[0082] The upper limit of the tin content is, for example, 0.005% by mass or less, for example, 0.003% by mass or less.

[0083] It is assumed that various pure titanium products and titanium alloy products can be obtained at low cost by using the metal titanium produced according to an embodiment of the present invention.

(Other Embodiments)

[0084] Other embodiments will be described below. In the embodiments described below, different points from the above embodiments will be mainly described. That is, the configurations described in the above embodiments can be appropriately applied to the following embodiments.

[0085] In the embodiments shown in Figs. 1(A) to (D), the anodes and the cathode are arranged at approximately the same height, but the rough electrodeposition step and the refinement electrodeposition steps can be performed even if the arrangement of the anodes and the cathode is changed. As an example, an embodiment where the cathode is arranged on the upper side and the anode is arranged on the lower side will be described below. As shown in Fig. 2(A), in an electrolytic device 200, for example, a nickel base BS is placed on the bottom of an electrolytic bath 210, and a TiAlO conductive material as an anode 220 is placed on the base BS, and a titanium cathode 230 is placed at a higher position than the anode 220. The control mechanism then supplies current to the anode 220 and the cathode 230 via electrically conductive lines EL connected to the base BS and the cathode 230, thereby performing molten salt electrolysis (rough electrodeposition step).

[0086] Subsequently, as shown in Fig. 2(B), the anode 220 is consumed as the anode 220 is eluted into the chloride bath Bf to form a titanium-containing electrodeposit TC having a reduced impurity content on the surface of the cathode 230. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0087] The titanium-containing electrodeposit TC formed on the surface of the cathode 230 taken out from the electrolytic bath 210 is then recovered by peeling it with a cutting tool. It should be noted that the titanium-containing electrodeposit TC may be washed and dried as described above.

[0088] Subsequently, as shown in Fig. 2(C), the nickel base BS is placed on the bottom of the electrolytic bath 210 and the titanium-containing electrodeposit TC as the anode 222 are placed on the base BS, and the titanium cathode 230 is placed at a higher position than the anode 222. The control mechanism then supplies current to the anode 222 and the cathode 230 via the electrically conductive lines EL connected to the base BS and the cathode 230, thereby performing the molten salt electrolysis (refinement electrodeposition step).

[0089] Subsequently, as shown in Fig. 2(D), the anode 222 is consumed as the anode 222 containing titanium is eluted into the chloride bath Bf to form a metal titanium electrodeposit TP having a reduced impurity content on the surface of the cathode 230. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0090] The cathode 230 is then taken out from the electrolytic bath 210, and the metal titanium electrodeposit TP

formed on the surface of the cathode 230 is washed, peeled, and dried to obtain metal titanium.

[0091] The embodiment shown in Fig. 3 is an embodiment where at least a part of the electrolytic bath is made of nickel and the portion made of nickel is used as the cathode. Further, it is an embodiment where the metal titanium can be produced without taking out the titanium-containing electrodeposit TC from the chloride bath Bf. As shown in Fig. 3(A), a nickel basket BK in which a TiAlO conductive material as an anode 320 is placed is arranged in an electrolytic device 300. In this case, by forming at least an inner wall of the electrolytic bath 310 from nickel, the inner wall serves as the cathode 330 during the molten salt electrolysis. The control mechanism then supplies current to the anode 320 and the cathode 330 via the electrically conductive lines EL connected to the basket BK and the cathode 330, thereby performing molten salt electrolysis (rough electrodeposition step).

[0092] Subsequently, as shown in Fig. 3(B), the anode 320 is consumed as the anode 320 is eluted into the chloride bath Bf to form a titanium-containing electrodeposit TC having a reduced impurity content on the inner wall of the electrolytic bath 310. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0093] The nickel basket BK is then taken out from the chloride bath Bf.

[0094] Subsequently, as shown in Fig. 3(C), a titanium cathode 335 is placed in the chloride bath Bf. In this case, the titanium-containing electrodeposit TC formed on the inner wall surface of the nickel electrolytic bath 310 is used as the anode 322. The control mechanism then supplies current to the anode 322 and the cathode 335 via the electrically conductive lines EL connected to the inner wall of the electrolytic bath 310 and the cathode 335, thereby performing molten salt electrolysis (refinement electrodeposition step).

[0095] Subsequently, as shown in Fig. 3(D), the anode 322 is consumed as the anode 322 is eluted into the chloride bath Bf to form a metal titanium electrodeposit TP having a reduced impurity content on the surface of the cathode 335. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0096] The cathode 335 is then taken out from the electrolytic bath 310, and the metal titanium electrodeposit TP formed on the surface of the cathode 335 is washed, peeled off, and dried to obtain metal titanium.

[0097] Yet another embodiment is described in which metal titanium can be produced without removing the titanium-containing electrodeposit TC from the chloride bath Bf. As shown in Fig. 4(A), nickel baskets BK each having a TiAlO conductive material placed as an anode 420 are arranged in an electrolytic device 400. Two titanium cathodes 430 and 435 are then arranged side by side toward the center from the positions where the baskets BK are arranged. In this embodiment, the titanium cathode 430 preferably has a large number of holes having openings on the anode 420 side and the titanium cathode 435 side, in terms of efficiency of electrodeposition. The shapes of the holes are not particularly limited, and they may be through holes each having a linear cross section, or holes each having a complicated shape such as that of a porous body. The molten salt electrolysis is then carried out by supplying electric current to the anodes 420 and the cathode 430 via the electrically conductive lines EL to the basket BK and the cathode 430 to which the control mechanism is connected (rough electrodeposition step).

[0098] Subsequently, as shown in Fig. 4(B), the anodes 420 are consumed as the anodes 420 are eluted into the chloride bath Bf to form a titanium-containing electrodeposit TC having a reduced impurity content on the surface of the cathode 430. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0099] Subsequently, as shown in Fig. 4(C), the cathodes 430 (see Fig. 4(B)) each having the titanium-containing electrodeposit TC formed on the surface is switched to the anodes 424, and the current is supplied to the anodes 424 whose control mechanism has been switched and the cathode 435 near the central portion, thereby performing molten salt electrolysis (refinement electrodeposition step). In this case, the titanium-containing electrodeposit TC becomes the anode 422.

[0100] Subsequently, as shown in Fig. 4(D), the anodes 422 and optionally the anode 424 are consumed as they are eluted into the chloride bath Bf to form metal titanium electrodeposit TP having a reduced impurity content on the surface of the cathode 435. The control mechanism then stops the current supply to terminate the molten salt electrolysis.

[0101] The cathode 435 is taken out from the electrolytic bath 410, and the metal titanium electrodeposit TP formed on the surface of the cathode 435 is washed, peeled off, and dried to obtain metal titanium.

[0102] An embodiment will be described in which multiple electrodeposition steps are continuously performed without taking out the titanium-containing electrodeposit TC from the chloride bath Bf and without changing the power supply connection. As shown in Fig. 5(A), an electrolytic device 500 is provided with a nickel basket BK in which a TiAlO conductive material as an anode 520 is placed, a titanium cathode 530, and a titanium bipolar electrode 540 at the center. Although the titanium bipolar electrode 540 is illustrated as being thick in Fig. 5A, the titanium bipolar electrode 540 may be thin. The control mechanism supplies current to the anode 520 and the cathode 530 via the electrically conductive lines EL connected to the basket BK and the cathode 530, thereby performing molten salt electrolysis.

[0103] Subsequently, as shown in Fig. 5(B), the anode 520 is consumed as the anode 520 is eluted into the chloride bath Bf to form a titanium-containing electrodeposit TC having a reduced impurity content on the surface of the bipolar electrode 540. The formation of the titanium-containing electrodeposit TC on the bipolar electrode 540 corresponds to the rough electrodeposition step.

[0104] In addition, since the current is flowing between the anode and the cathode, the dissolution of the anode and

the dissolution of the bipolar electrode can proceed at the same time. Fig. 5(C) shows that the cathode 530 side of the bipolar electrode 540 is eluted. In this embodiment, the bipolar electrode 540 will first elute titanium derived from the bipolar electrode 540 and then the titanium-containing electrodeposit TC.

[0105] Subsequently, as shown in Fig. 5(D), the bipolar electrode 540 and the titanium-containing electrodeposit TC are consumed to form a metal titanium electrodeposit TP having a reduced impurity content on the surface of the cathode 530 (refinement electrodeposition step). The current supply is then stopped in order to terminate the molten salt electrolysis.

[0106] The cathode 530 is then taken out from the electrolytic bath 510, and the metal titanium electrodeposit TP formed on the surface of the cathode 530 is washed, peeled off, and dried to obtain metal titanium.

[0107] In Fig. 5(A), the titanium bipolar electrode is arranged. However, for example, the titanium-containing electrodeposit TC obtained by subjecting a TiAlO conductive material to molten salt electrolysis is arranged instead of the bipolar electrode, and the titanium-containing electrodeposit TC may be used as a bipolar electrode.

[0108] Alternatively, for example, after the titanium-containing electrodeposit TC is formed on the surface of the bipolar electrode 540 on the anode 520 side, a hook (not shown) attached to the upper end of the bipolar electrode 540 may be hooked with a hanging rod or the like to rotate the bipolar electrode 540 at 180 degrees. By doing so, the titanium-containing electrodeposit TC faces the cathode 530.

[0109] Although the above descriptions show that the bipolar electrode and the cathode are made of titanium, the material can be appropriately changed as long as the electrodeposit can be deposited. In addition, the bipolar electrode should have conductivity. Therefore, any non-conductive material such as ceramics cannot be used for the bipolar electrode.

[0110] As described above, the bipolar electrode may be non-movable or movable. Since electrodeposition and elution can occur simultaneously in the case of the non-movable bipolar electrode, it is preferable to have a large number of pores opening to the anode side and the cathode side. On the other hand, in the case of the movable bipolar electrode, electrodeposition and elution can proceed separately, so that the pores as described above are not necessary. Rather, elimination of the pores can avoid situations where the electrodeposit enters the pores and require a long period of time for elution.

[0111] As described above, the multiple rough electrodeposition steps and refinement electrodeposition steps have been described. These can be carried out in combination as appropriate. For example, after carrying out the rough electrodeposition step according to the embodiment shown in Figs 1(A) and (B), the refinement electrodeposition steps according to the embodiment shown in Figs. 2(C) and (D) can also be carried out.

[2. Metal Titanium Electrodeposit]

[0112] The metal titanium electrodeposit according to the present invention can be produced by the method for producing metal titanium described above, and has a reduced impurity content. The metal titanium electrodeposit has a low impurity content, and, for example, the total impurity content is 3000 ppm by mass or less. In an embodiment, the metal titanium electrodeposit has a composition having an aluminum content of 5 ppm by mass or more and 100 ppm by mass or less, and an oxygen content of 100 ppm by mass or more and 500 ppm by mass or less, the balance being titanium and unavoidable impurities. These unavoidable impurities are often ore-derived impurities and chloride bath-derived components. The content of each of the above components can also be within the range described above in "Composition of Metal Titanium".

[0113] Also, in an embodiment, the above unavoidable impurities and the like may be more specifically identified. That is, the nitrogen content in the metal titanium electrodeposit may be 0.001% by mass or more and 0.03% by mass or less, and the carbon content may be 0.0004% by mass or more and 0.01 % by mass or less, the iron content may be 0.010% by mass or less, the magnesium content may be 0.05% by mass or less, the nickel content may be 0.01 % by mass or less, the chromium content may be 0.005% by mass or less, the silicon content may be 0.001% by mass or less, the manganese content may be 0.05% by mass or less, and the tin content may be 0.01 % by mass or less. The content of each of the above components can also be within the range described above in "Composition of Metal Titanium".

[0114] It should be noted that the method for measuring the impurity content of each component of the metal titanium electrodeposit is the same as the method for measuring the impurity content of each component of the TiAlO conductive material as described above.

(Sieving)

[0115] In a further embodiment, the particle size distribution of the metal titanium electrodeposit is not particularly limited, but it is such that a ratio of particle sizes of the metal titanium electrodeposit on the sieve when it is sieved through a 300 μm mesh sieve is, on a mass basis, for example, 60% or more, for example 70% or more, as a lower limit. Further, the upper limit of the ratio of the particle sizes of the metal titanium electrodeposit on the sieve is, for

example, 90% or less, for example, 85% or less.

[0116] An example of the method for measuring the particle size distribution by sieving is shown below.

[0117] In a glove box in an argon atmosphere with an oxygen concentration of 5% by volume or less, the metal titanium electrodeposit is cracked to the extent that it is not crushed or pulverized, and sieved using a sieve with an opening of 300 μm . As shown in the following equation (1), a mass (A_1) of the metal titanium electrodeposit on the sieve having an opening of 300 μm is divided by the total mass (A_{total}) introduced into the sieve, and a ratio (α) is calculated as a percentage:

$$\alpha (\%) = A_1 (\text{g}) / A_{\text{total}} \times 100$$

[Examples]

[0118] The present invention will be specifically described based on Examples and Comparative examples. The descriptions of the following Examples and Comparative examples are merely experimental specific examples for facilitating the understanding of the technical content of the present invention, and the technical scope of the present invention is not limited by these specific examples.

[Evaluation of TiAlO Conductive Material]

[0119] First, the TiAlO conductive materials used in Examples and Comparative Examples described below were prepared by heating chemical blends including titanium ore containing titanium oxide, aluminum, and calcium fluoride as a separating agent under conditions as described below, followed by a post-process according to a known method (extraction process). In the extraction process, the amounts of titanium ore, aluminum and separating agent introduced were adjusted so that the molar ratio of titanium oxide: aluminum: separating agent was in the range of 3:4-7:2-6. The impurity content of each component of each measuring sample collected from the TiAlO conductive materials was measured by ICP emission spectrometry (PS3520UVDDII, manufactured by HITACHI) for metal components, by an inert gas fusion-infrared absorption method (TC-436AR, manufactured by LECO) for oxygen, by an inert gas fusion-thermal conductivity method (TC-436AR, manufactured by LECO) for nitrogen, and by a combustion-infrared absorption method (EMIA-920V2, manufactured by Horiba, Ltd.) for carbon. This method for measuring the content of each component is also applied to the titanium-containing electrodeposit, the metal titanium, and the metal titanium electrodeposit. Further, a specific resistance of a separate measuring sample collected in the form of a 10 mm square block was measured by a two-terminal measurement method (low resistance meter 3566-RY, manufactured by Tsuruga Electric Corporation). These results are shown in Table 1.

<Production Conditions for TiAlO Conductive Material>

[0120]

Titanium ore: titanium oxide content of 95% by mass;
Inert gas: argon gas; and
Heating temperature: 1500°C to 1800°C.

[Table 1]

	Al [% by mass]	O [% by mass]	N [% by mass]	C [% by mass]	Fe [% by mass]	Mg [% by mass]	Ni [% by mass]	Cr [% by mass]	Si (% by mass]	Mn [% by mass]	Sn [% by mass]
TiAlO Conductive Material	11.6	10.3	0.004	0.69	2.23	<0.001	<0.001	0.08	0.736	0.006	0.002

[Table 2]

	Specific Resistance [$\Omega \cdot m$]
TiAlO Conductive Material	5×10^{-5}

[Production of Metal Titanium]

<Example 1>

(Rough Electrodeposition)

[0121] An electrolytic device 600 having the structure shown in Figs. 6(A) and 7 was used. The dimensions and shape of the bath portion of the electrolytic bath 610 of the electrolytic device 600 were $300 \text{ mm}\Phi \times 570 \text{ mm}$ in depth. Subsequently, 30 kg of magnesium chloride (see Table 3) was introduced into the electrolytic bath 610 of the electrolytic device 600 and dissolved to obtain a chloride bath Bf. Annular nickel baskets BK each having an anode 620 made of 5000 g of TiAlO conductive material were then arranged. A titanium round bar having a diameter $50 \text{ mm} \times 300 \text{ mm}$ was prepared as a cathode 630. The anodes 620 and the cathode 630 were arranged such that the height direction of each anode 620 and the cathode 630 was substantially parallel to the depth direction of the chloride bath.

[0122] The control mechanism supplied electric current to the anodes 620 and the cathode 630 via the electrically conductive lines EL connected to the anodes 620 and the cathode 630 to perform molten salt electrolysis in the chloride bath Bf. After seven hours from the start of the current supply, the control mechanism stopped the current supply. It should be noted that, as shown in Fig. 6(B), a titanium-containing electrodeposit TC deposited over the entire surface of the cathode 630 was obtained.

<Electrolysis Conditions>

[0123]

Interior of electrolytic bath: Ar gas atmosphere;
Temperature of chloride bath: 850°C ; and
Current density: 0.5 A/cm^2 .

[0124] After stopping the current supply, the cathode 630 was pulled out of the electrolytic bath 610, and the cathode 630 and the titanium-containing electrodeposit TC were washed with water to remove adhering molten salts. The titanium-containing electrodeposit TC containing metal titanium was peeled off from the cathode 630 with a cutting tool and recovered. Moisture was evaporated from the titanium-containing electrodeposit TC by vacuum separation.

[0125] A measuring sample collected from the titanium-containing electrodeposit TC obtained by the rough electrodeposition was measured for the impurity content of each component by the method as described above. The results are shown in Table 4.

[0126] Further, the ratio of the titanium-containing electrodeposit TC on the sieve was measured by a sieving method (using a sieve having an opening of $300 \mu\text{m}$).

[0127] Further, the shape of the titanium-containing electrodeposit TC was confirmed by taking it by a camera. In order to confirm the shape of the titanium-containing electrodeposit TC, SEM observation was performed under the following measurement conditions. These results are shown in Figs. 8(A) and (B).

<SEM Measurement Conditions>

[0128]

SEM: model JSM-7800F, manufactured by JEOL;
Acceleration voltage: 10 kV ; and
Magnifications: in range of 60 to 1000 times.

(Refinement Electrodeposition)

[0129] As shown in Fig. 6(C), 30 kg of magnesium chloride (see Table 3) was introduced into the electrolytic bath 610

of the electrolytic device 600 and dissolved to obtain a chloride bath Bf. Ring shaped nickel baskets BK each having an anode 622 made of 500 g of titanium-containing electrodeposit TC were then arranged. A titanium round bar having a diameter of 50 mm × 300 mm was prepared as a cathode 630. The anodes 622 and the cathode 630 were arranged such that the height direction of each anode 622 and the cathode 630 was substantially parallel to the depth direction of the chloride bath.

[0130] The control mechanism supplied electric current to the anodes 622 and the cathode 630 via the electrically conductive lines EL connected to the anodes 622 and the cathode 630 to perform molten salt electrolysis in the chloride bath Bf. After two hours from the start of the current supply, the control mechanism stopped the current supply. Further, as shown in Fig. 6(D), a metal titanium electrodeposit TP deposited over the entire surface of the cathode 130 was obtained.

<Electrolysis Conditions>

[0131]

Interior of electrolytic cell: Ar gas atmosphere;
Temperature of chloride bath: 850°C; and
Current density: 0.5 A/cm².

[0132] After stopping the current supply, the cathode 130 was pulled out from the electrolytic bath 110, and the cathode 130 and the metal titanium electrodeposit TP were washed with an acid and then washed with water to remove adhering molten salts. The metal titanium electrodeposit TP was peeled off from the cathode 130 with a cutting tool and recovered. Moisture was evaporated from the metal titanium electrodeposit TP by vacuum separation.

[0133] A measuring sample collected from the metal titanium electrodeposit TP obtained by the refinement electrodeposition was measured for the impurity content of each component by the method as described above. The results are shown in Table 4.

[0134] Further, the ratio of the metal titanium electrodeposit TP on the sieve was measured by a sieving method (using a sieve having a sieve opening of 300 μm). These results are shown in Table 5.

[0135] Further, the shape of the metal titanium TP was confirmed by taking it by a camera. In order to confirm the shape of the metal titanium electrodeposit TP, SEM observation was performed under the following measurement conditions. These results are shown in Figs. 9(A) and (B).

<SEM Measurement Conditions>

[0136]

SEM: model JSM-7800F, manufactured by JEOL;
Acceleration voltage: 10 kV; and
Magnifications: in range of 60 to 1000 times.

<Examples 2 to 6, Comparative Examples 1 to 3>

[0137] Examples 2 to 6 and Comparative Examples 1 to 3 were carried out by the same method as that of Example 1, with the exception that the chloride bath was changed to that shown in Table 3. It should be noted that only Example 6 was subjected to two refinement electrodeposition steps. After the electrodeposits prepared in each step were washed with water and vacuum-dried in the same manner as in Example 1, the contents of impurities and the percentages of sieved deposits were measured. The results are shown in Tables 4 and 5.

[Table 3]

	Rough Electrodeposition Chloride Bath Composition [mol%]	First Refinement Electrodeposition Chloride Bath Composition [mol%]	Second Refinement Electrodeposition Chloride Bath Composition [mol%]
Example 1	100%MgCl₂	100%MgCl₂	-
Example 2	50%NaCl-50%KCl	100%MgCl₂	-
Example 3	100%MgCl₂	50%NaCl-50%KCl	-

(continued)

	Rough Electrodeposition Chloride Bath Composition [mol%]	First Refinement Electrodeposition Chloride Bath Composition [mol%]	Second Refinement Electrodeposition Chloride Bath Composition [mol%]
Example 4	30%MgCl₂-35%NaCl- 35%KCl	100%MgCl₂	-
Example 5	80%MgCl₂-10%NaCl- 10%KCl	80%MgCl₂-10%NaCl-10%KCl	-
Example 6	50%MgCl₂-25%NaCl- 25%KCl	50%MgCl₂-25%NaCl-25%KCl	50%MgCl₂-25%NaCl-25%KCl
Comparative Example 1	50%NaCl-50%KCl	50%NaCl-50%KCl	-
Comparative Example 2	10%MgCl₂-45%NaCl- 45%KCl	10%MgCl₂-45%NaCl-45%KCl	-
Comparative Examples	50%NaCl-50%KCl	20%MgCl₂-40%NaCl-40%KCl	-

[Table 4]

	Al [ppm by mass]	O [ppm by mass]	N [% by mass]	C [% by mass]	Fe [% by mass]	Mg [% by mass]	Ni [% by mass]	Cr [% by mass]	Si [% by mass]	Mn [% by mass]	Sn [% by mass]
Example 1	Electrodeposit after Rough Electrodeposition	2120	10400	0.02	0.004	0.007	0.03	0.03	0.002	0.02	<0.001
	Electrodeposit after 1st Ref. Electrodeposition	30	310	0.006	0.001	<0.001	<0.001	0.004	<0.001	0.009	<0.001
Example 2	Electrodeposit after Rough Electrodeposition	11000	9380	0.02	0.004	0.005	<0.001	0.03	0.002	0.03	<0.001
	Electrodeposit after 1st Ref. Electrodeposition	90	410	0.007	0.001	<0.001	<0.001	0.005	<0.001	0.01	<0.001
Example 3	Electrodeposit after Rough Electrodeposition	2120	10400	0.02	0.004	0.007	<0.001	0.03	0.002	0.02	<0.001
	Electrodeposit after 1st Ref. Electrodeposition	90	400	0.007	0.001	<0.001	<0.001	0.004	<0.001	0.01	<0.001
Example 4	Electrodeposit after Rough Electrodeposition	7100	1110	0.03	0.005	0.005	<0.001	0.04	0.001	0.03	<0.001
	Electrodeposit after 1st Ref. Electrodeposition	90	310	0.008	0.001	<0.001	<0.001	0.005	<0.001	0.009	<0.001
Example 5	Electrodeposit after Rough Electrodeposition	4070	12000	0.01	0.004	0.006	<0.001	0.04	0.002	0.02	<0.001
	Electrodeposit after 1st Ref. Electrodeposition	80	430	0.005	0.001	<0.001	<0.001	0.005	<0.001	0.01	<0.001

(continued)

		Al [ppm by mass]	O [ppm by mass]	N [% by mass]	C [% by mass]	Fe [% by mass]	Mg [% by mass]	Ni [% by mass]	Cr [% by mass]	Si [% by mass]	Mn [% by mass]	Sn [% by mass]
Example 6	Electrodeposition after Rough Electrodeposition	5240	11300	0.01	0.04	0.006	0.01	<0.001	0.04	0.001	0.02	<0.001
	Electrodeposition after 1st Ref. Electrodeposition	100	420	0.007	0.001	<0.001	0.009	<0.001	0.006	<0.001	0.01	<0.001
Comparative Example 1	Electrodeposition after 2nd Ref. Electrodeposition	40	100	0.002	<0.001	<0.001	0.009	<0.001	0.001	<0.001	0.008	<0.001
	Electrodeposition after Rough Electrodeposition	11000	9380	0.02	0.004	0.005	<0.001	<0.001	0.03	0.002	0.03	<0.001
Comparative Example 2	Electrodeposition after 1st Ref. Electrodeposition	710	330	0.006	0.001	<0.001	<0.001	<0.001	0.003	<0.001	0.008	<0.001
	Electrodeposition after Rough Electrodeposition	8180	10100	0.03	0.005	0.005	0.005	<0.001	0.04	0.001	0.03	<0.001
Comparative Example 3	Electrodeposition after 1st Ref. Electrodeposition	520	310	0.005	0.001	<0.001	0.004	<0.001	0.004	<0.001	0.001	<0.001
	Electrodeposition after Rough Electrodeposition	11000	9380	0.02	0.004	0.005	<0.001	<0.001	0.03	0.002	0.03	<0.001
Comparative Example 3	Electrodeposition after 1st Ref. Electrodeposition	620	320	0.004	0.001	<0.001	0.006	<0.001	0.005	<0.001	0.008	<0.001
	Electrodeposition after Rough Electrodeposition	11000	9380	0.02	0.004	0.005	<0.001	<0.001	0.03	0.002	0.03	<0.001

[Table 5]

		Ratio of Particles larger than 300 μm [%] (mass)
5	Example 1	Electrodeposit after Rough Electrodeposition 42
		Electrodeposit after 1st Ref. Electrodeposition 82
10	Example 2	Electrodeposit after Rough Electrodeposition 16
		Electrodeposit after 1st Ref. Electrodeposition 78
15	Example 3	Electrodeposit after Rough Electrodeposition 42
		Electrodeposit after 1st Ref. Electrodeposition 70
20	Example 4	Electrodeposit after Rough Electrodeposition 25
		Electrodeposit after 1st Ref. Electrodeposition 62
25	Example 5	Electrodeposit after Rough Electrodeposition 40
		Electrodeposit after 1st Ref. Electrodeposition 61
30	Example 6	Electrodeposit after Rough Electrodeposition 31
		Electrodeposit after 1st Ref. Electrodeposition 61
		Electrodeposit after 2nd Ref. Electrodeposition 75
35	Compative Example 1	Electrodeposit after Rough Electrodeposition 19
		Electrodeposit after 1st Ref. Electrodeposition 40
40	Compative Example 2	Electrodeposit after Rough Electrodeposition 16
		Electrodeposit after 1st Ref. Electrodeposition 44
45	Compative Example 3	Electrodeposit after Rough Electrodeposition 16
		Electrodeposit after 1st Ref. Electrodeposition 42

(Discussion of Examples)

[0138] In Examples 1 to 6, the metal titanium electrodeposit TP finally obtained by molten salt electrolysis using the TiAlO conductive material having an aluminum content of 11.6% by mass and an oxygen content of 10.3% by mass could reduce the aluminum content to be less than or equal to 100 ppm by mass and the oxygen content to be less than

or equal to 500 ppm by mass. That is, as confirmed by Examples, it was effective that at least one of the chloride bath used for the rough electrodeposition and the chloride bath used for the refinement electrodeposition contained 30 mol % or more of magnesium chloride. Therefore, it is presumed that high-purity titanium metal can be produced by using such a titanium metal electrodeposit.

[0139] In particular, in Example 1, it is presumed that the chloride bath used for the rough electrodeposition and the chloride bath used for the refinement electrodeposition contained 100 mol% of magnesium chloride, so that the aluminum content and oxygen content could be more reliably reduced.

[0140] Further, in Example 6, it is presumed that the aluminum content and the oxygen content in the metal titanium electrodeposit TP could be more reliably reduced by performing the multiple refinement electrodeposition steps.

[0141] On the other hand, in Comparative Examples 1 to 3, neither the chloride bath used for the rough electrodeposition nor the chloride bath used for the refinement electrodeposition contained 30 mol% or more of magnesium chloride. Therefore, in Comparative Examples 1 to 3, it is presumed that the aluminum content could not be satisfactorily reduced.

[Description of Reference Numerals]

[0142]

100, 200, 300, 400, 500, 600 electrolytic device

110, 210, 310, 410, 510, 610 electrolytic bath

120, 122, 220, 222, 320, 322, 420, 422, 424, 520, 620, 622 anode

130, 230, 330, 335, 430, 435, 530, 630 cathode

540 bipolar electrode

Bf chloride bath

BK basket

BS base

EL electrically conductive line

TC titanium-containing electrodeposit

TP metal titanium electrodeposit

[0143] It is to understand that the present invention also includes the following inventions:

[1] A method for producing metal titanium, comprising: a refining process of refining a TiAlO conductive material containing titanium, aluminum, and oxygen, wherein the refining step comprises:

a rough electrodeposition process of performing a molten salt electrolysis using an electrode containing the TiAlO conductive material in a chloride bath to obtain a titanium-containing electrodeposit; and after the rough electrodeposition step, one or more refinement electrodeposition steps of performing a molten salt electrolysis using an electrode containing the titanium-containing electrodeposit in a chloride bath, and wherein at least one of the chloride bath used for the rough electrodeposition step and the chloride bath used for the refinement electrodeposition step contains 30 mol % or more of magnesium chloride.

[2] The method for producing metal titanium according to [1], wherein at least one of the chloride bath used for the rough electrodeposition step and the chloride bath used for the refinement electrodeposition step contains 50 mol % or more of magnesium chloride.

[3] The method for producing metal titanium according to [1], wherein each of the chloride bath used for the rough electrodeposition step and at least one chloride bath used for the refinement electrodeposition steps contains 30 mol % or more of magnesium chloride.

[4] The method for producing metal titanium according to [1], wherein each of the chloride bath used for the rough electrodeposition step and at least one chloride bath used for the refinement electrodeposition steps contains 50 mol % or more of magnesium chloride.

[5] The method for producing metal titanium according to any one of [1] to [4], further comprising an extracting process of heating a chemical blend comprising a titanium ore containing titanium oxide, aluminum, and a separating agent to obtain the TiAlO conductive material, before the refining process.

[6] The method for producing metal titanium according to [5], wherein a molar ratio of the titanium oxide, the aluminum and the separating agent contained in the chemical blend is 3:4-7:2-6.

[7] The method for producing metal titanium according to [5] or [6], wherein the separating agent comprises one or more selected from calcium fluoride, calcium oxide and sodium fluoride.

[8] The method for producing metal titanium according to any one of [1] to [7], wherein the metal titanium has an aluminum content of 100 ppm by mass or less and an oxygen content of 500 ppm by mass or less.

[9] The method for producing metal titanium according to [8], wherein the metal titanium has a nitrogen content of 0.03% by mass or less, a carbon content of 0.01 % by mass or less, an iron content of 0.010% by mass or less, a magnesium content of 0.05% by mass or less, a nickel content of 0.01 % by mass or less, a chromium content of 0.005% by mass or less, a silicon content of 0.001% by mass or less, a manganese content of 0.05% by mass or less, and a tin content of 0.01 % by mass or less.

[10] A metal titanium electrodeposit, wherein the metal titanium electrodeposit has an aluminum content of 5 ppm by mass or more and 100 ppm by mass or less, and an oxygen content of 100 ppm by mass or more and 500 ppm by mass or less.

[11] The metal titanium electrodeposit according to [10], wherein the metal titanium electrodeposit has a nitrogen content of 0.001% by mass or more and 0.03% by mass or less, a carbon content of 0.0004% by mass or more and 0.01 % by mass or less, an iron content of 0.010% by mass or less, a magnesium content of 0.05% by mass or less, a nickel content of 0.01 % by mass or less, a chromium content of 0.005% by mass or less, a silicon content of 0.001% by mass or less, a manganese content of 0.05% by mass or less, and a tin content of 0.01 % by mass or less.

Claims

1. A method for producing metal titanium, comprising: a refining process of refining a TiAlO conductive material containing titanium, aluminum, and oxygen, wherein the refining process comprises:

a rough electrodeposition step of performing a molten salt electrolysis using an electrode containing the TiAlO conductive material in a chloride bath to obtain a titanium-containing electrodeposit; and after the rough electrodeposition step, one or more refinement electrodeposition steps of performing a molten salt electrolysis using an electrode containing the titanium-containing electrodeposit in a chloride bath, and wherein at least one of the chloride bath used for the rough electrodeposition step and the chloride bath used for the refinement electrodeposition step contains 30 mol % or more of magnesium chloride.

2. The method for producing metal titanium according to claim 1, wherein at least one of the chloride bath used for the rough electrodeposition step and the chloride bath used for the refinement electrodeposition step contains 50 mol % or more of magnesium chloride.

3. The method for producing metal titanium according to claim 1, wherein each of the chloride bath used for the rough electrodeposition step and at least one chloride bath used for the refinement electrodeposition steps contains 30 mol % or more of magnesium chloride.

4. The method for producing metal titanium according to claim 1, wherein each of the chloride bath used for the rough electrodeposition step and at least one chloride bath used for the refinement electrodeposition steps contains 50 mol % or more of magnesium chloride.

5. The method for producing metal titanium according to any one of claims 1 to 4, further comprising an extracting process of heating a chemical blend comprising a titanium ore containing titanium oxide, aluminum, and a separating agent to obtain the TiAlO conductive material, before the refining process.

6. The method for producing metal titanium according to claim 5, wherein a molar ratio of the titanium oxide, the aluminum and the separating agent contained in the chemical blend is 3:4-7:2-6.

7. The method for producing metal titanium according to claim 5 or 6, wherein the separating agent comprises one or more selected from calcium fluoride, calcium oxide and sodium fluoride.

8. The method for producing metal titanium according to any one of claims 1 to 7, wherein the metal titanium has an aluminum content of 100 ppm by mass or less and an oxygen content of 500 ppm by mass or less.

9. The method for producing metal titanium according to claim 8, wherein the metal titanium has a nitrogen content of 0.03% by mass or less, a carbon content of 0.01% by mass or less, an iron content of 0.010% by mass or less, a magnesium content of 0.05% by mass or less, a nickel content of 0.01% by mass or less, a chromium content of

0.005% by mass or less, a silicon content of 0.001% by mass or less, a manganese content of 0.05% by mass or less, and a tin content of 0.01 % by mass or less.

5 **10.** A metal titanium electrodeposit, wherein the metal titanium electrodeposit has an aluminum content of 5 ppm by mass or more and 100 ppm by mass or less, and an oxygen content of 100 ppm by mass or more and 500 ppm by mass or less.

10 **11.** The metal titanium electrodeposit according to claim 10, wherein the metal titanium electrodeposit has a nitrogen content of 0.001% by mass or more and 0.03% by mass or less, a carbon content of 0.0004% by mass or more and 0.01% by mass or less, an iron content of 0.010% by mass or less, a magnesium content of 0.05% by mass or less, a nickel content of 0.01% by mass or less, a chromium content of 0.005% by mass or less, a silicon content of 0.001% by mass or less, a manganese content of 0.05% by mass or less, and a tin content of 0.01 % by mass or less.

15

20

25

30

35

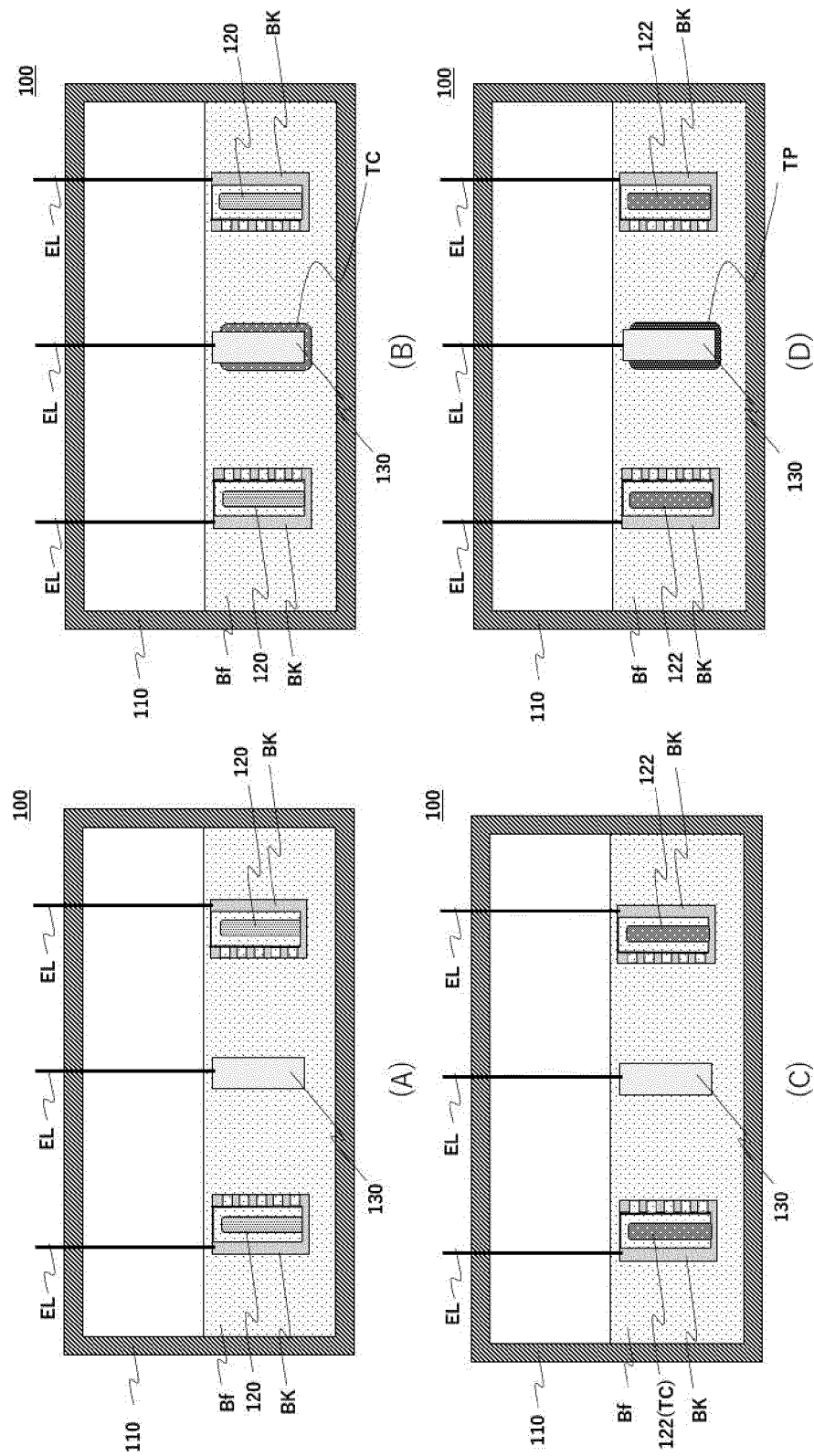
40

45

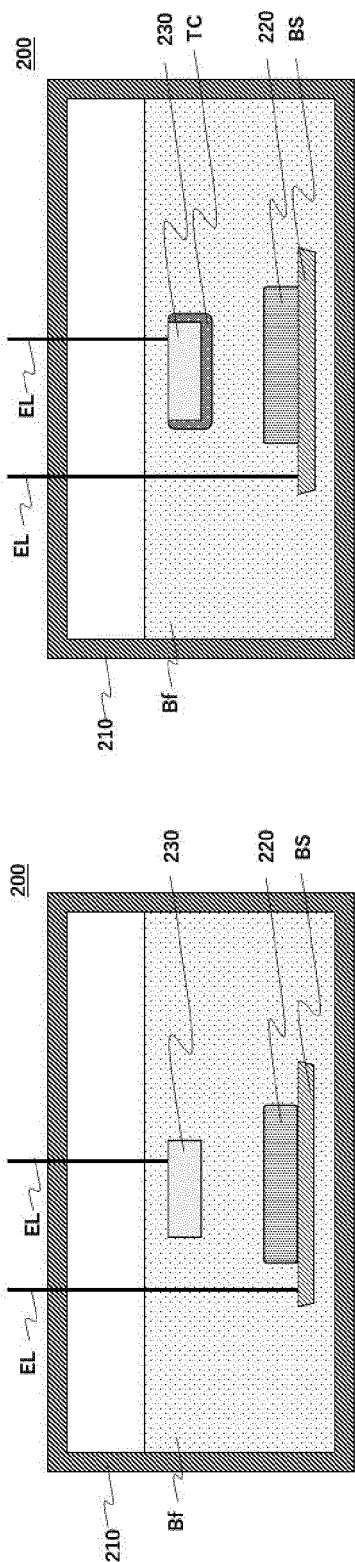
50

55

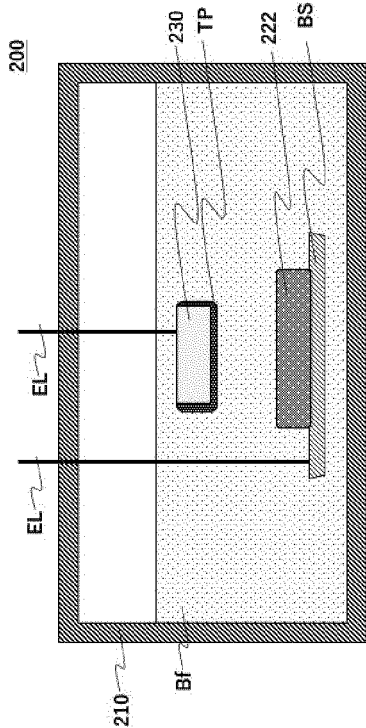
[Fig. 1]



[Fig. 2]

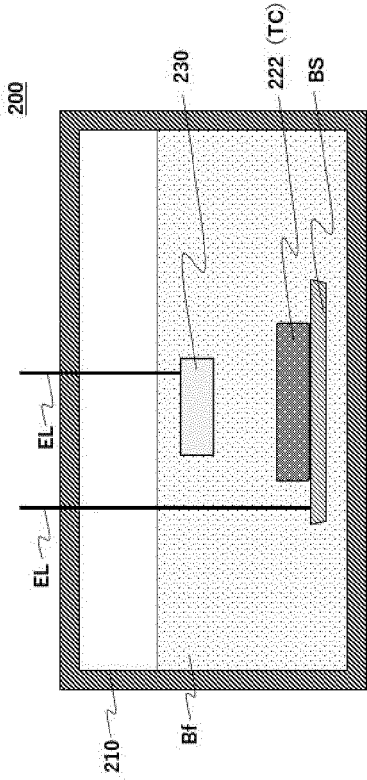


(B)



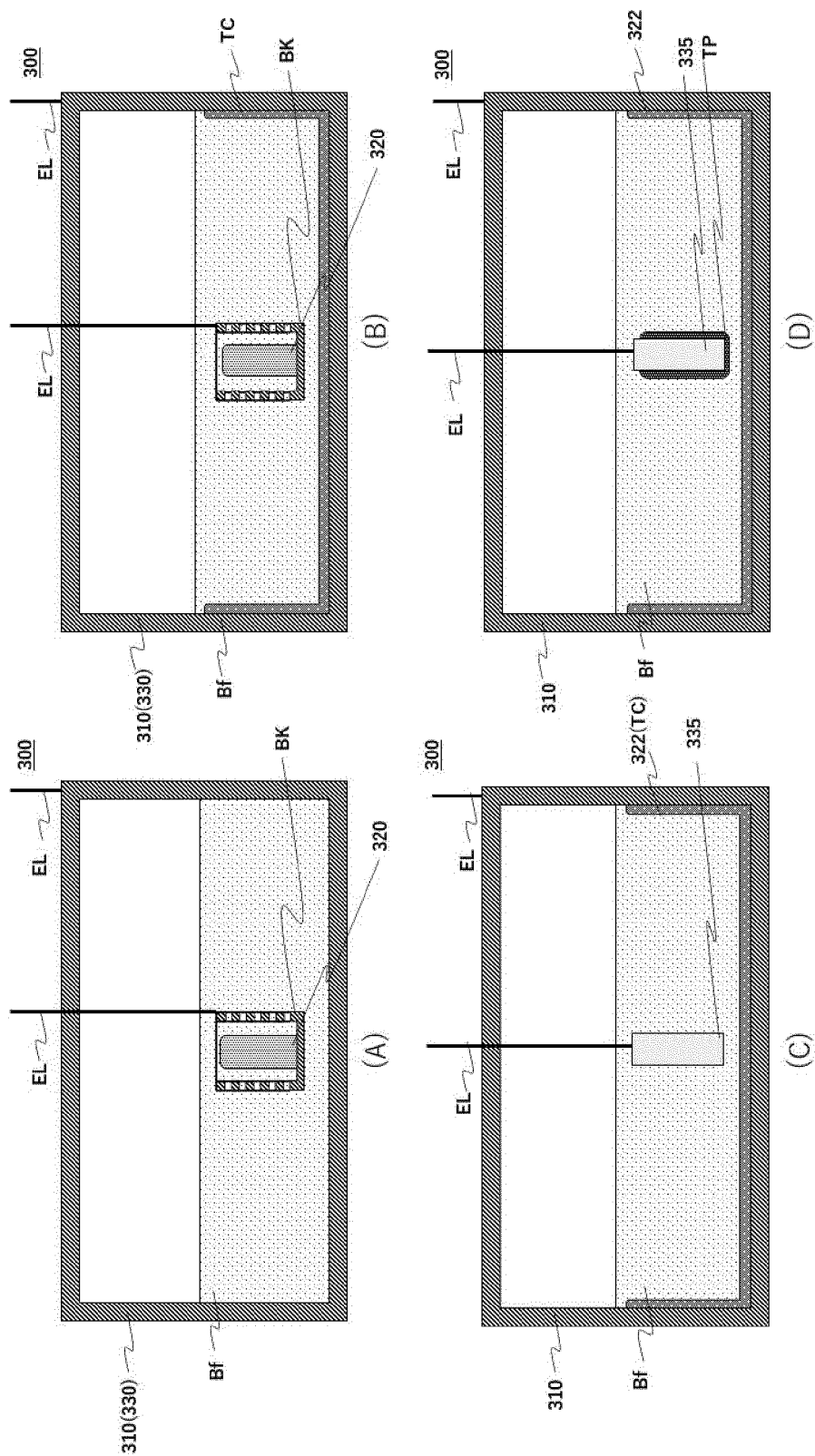
(D)

(A)

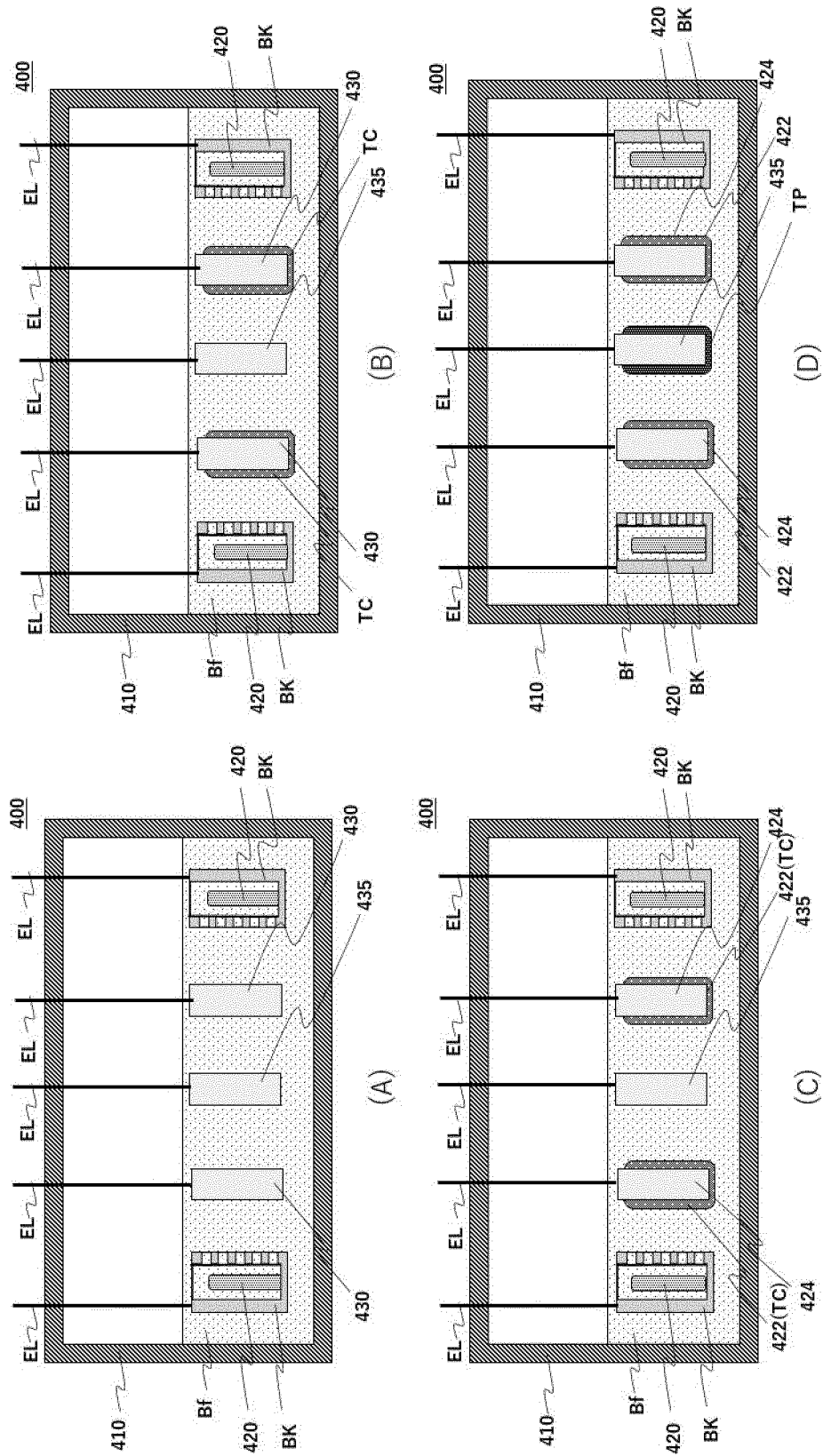


(C)

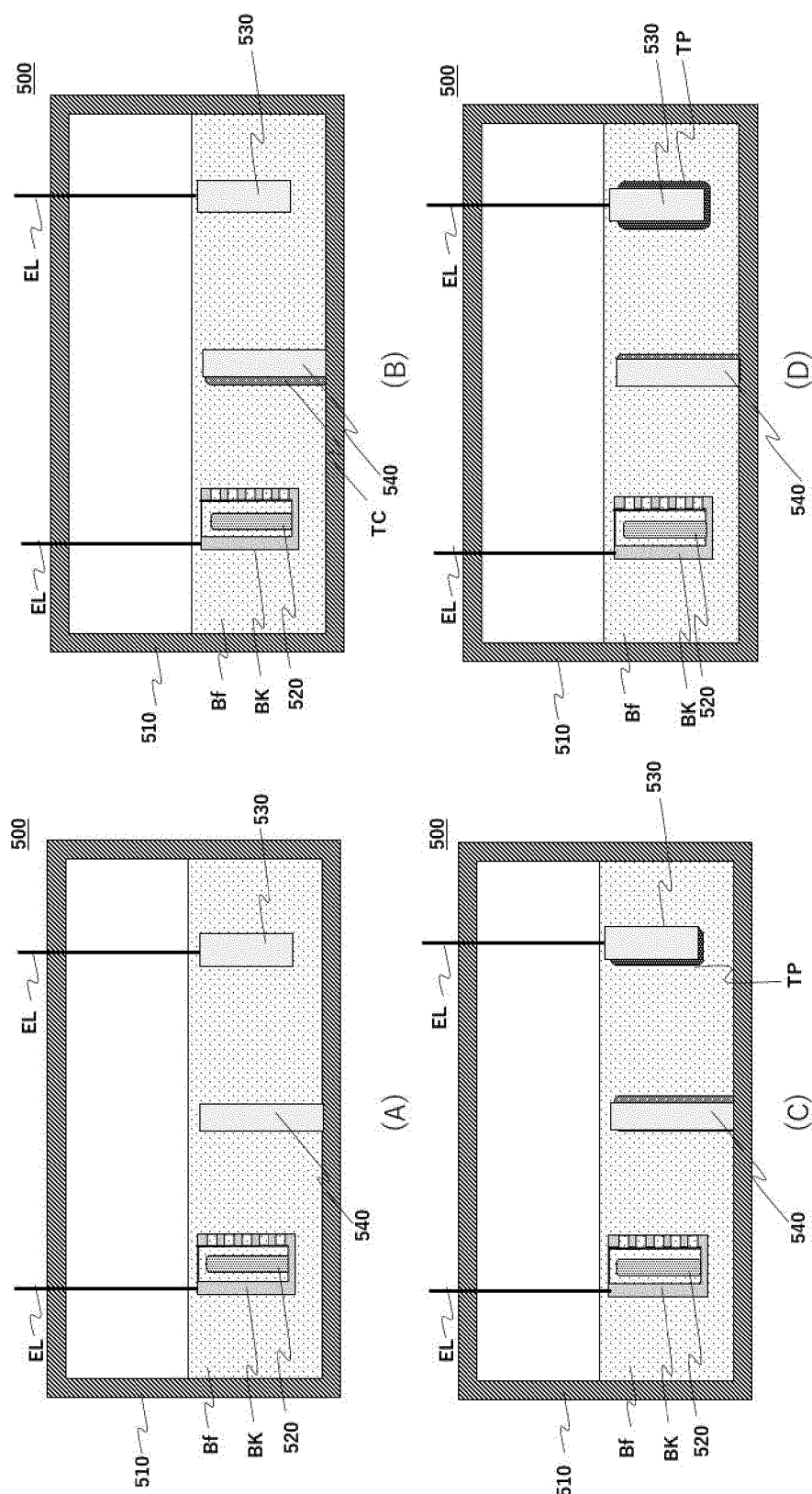
[Fig. 3]



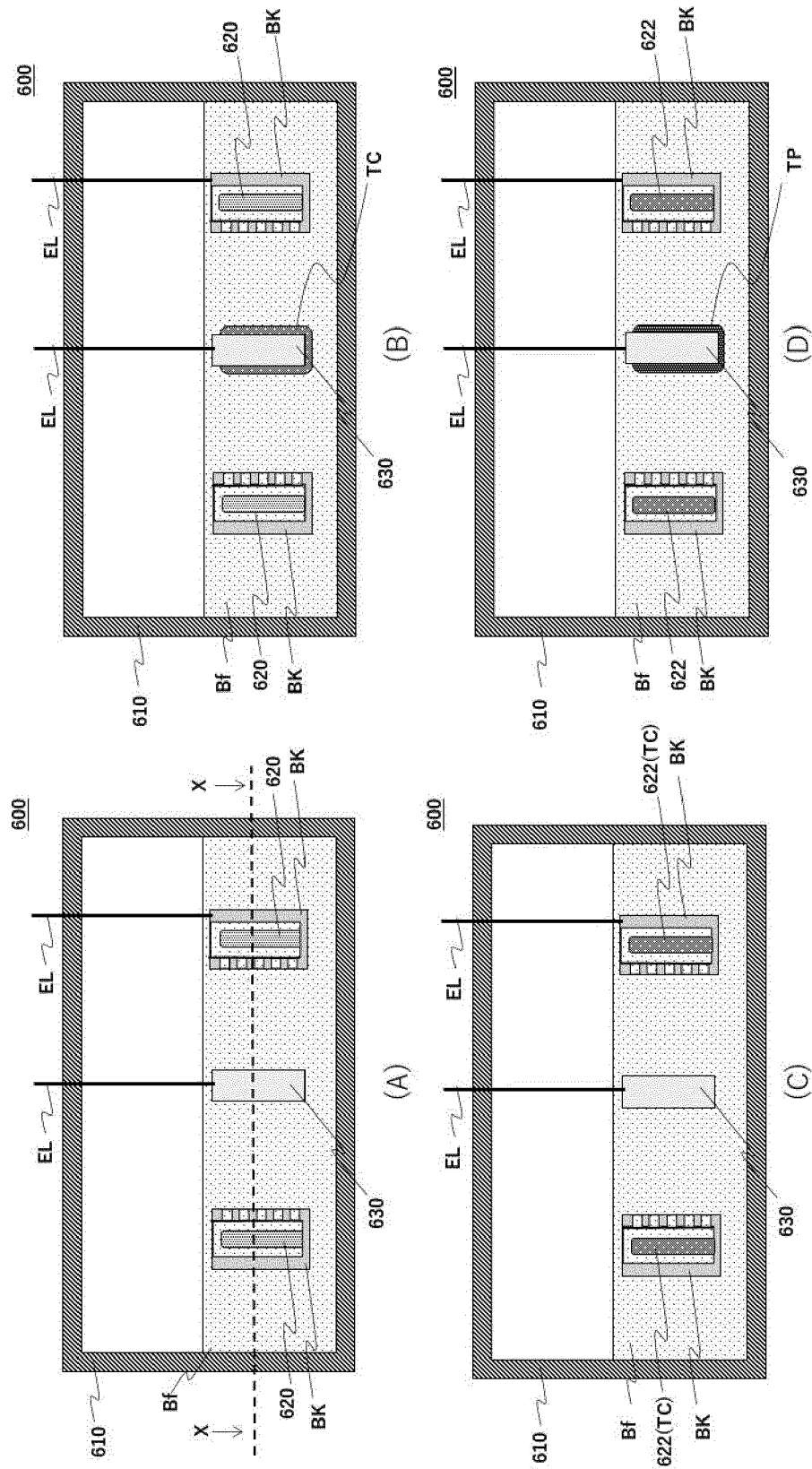
[Fig. 4]



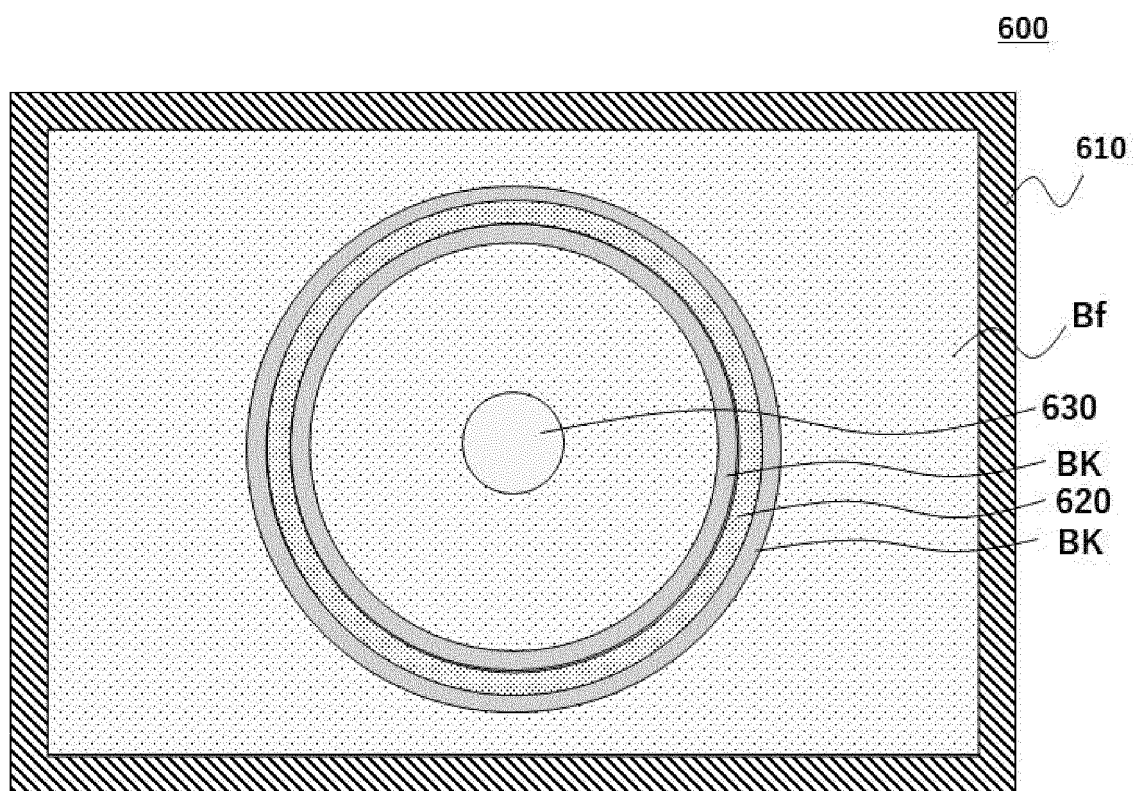
[Fig. 5]



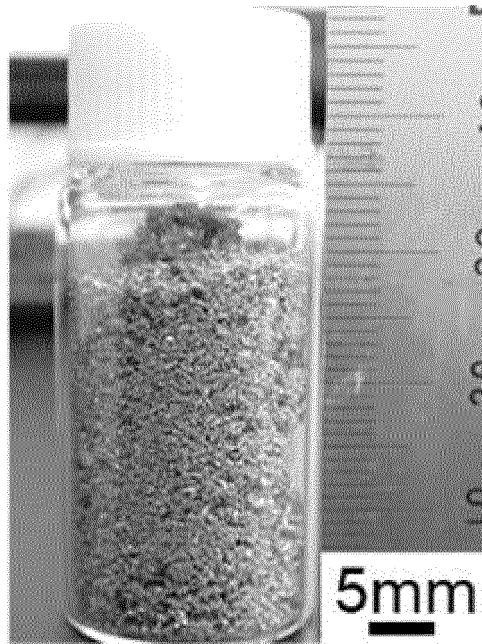
[Fig. 6]



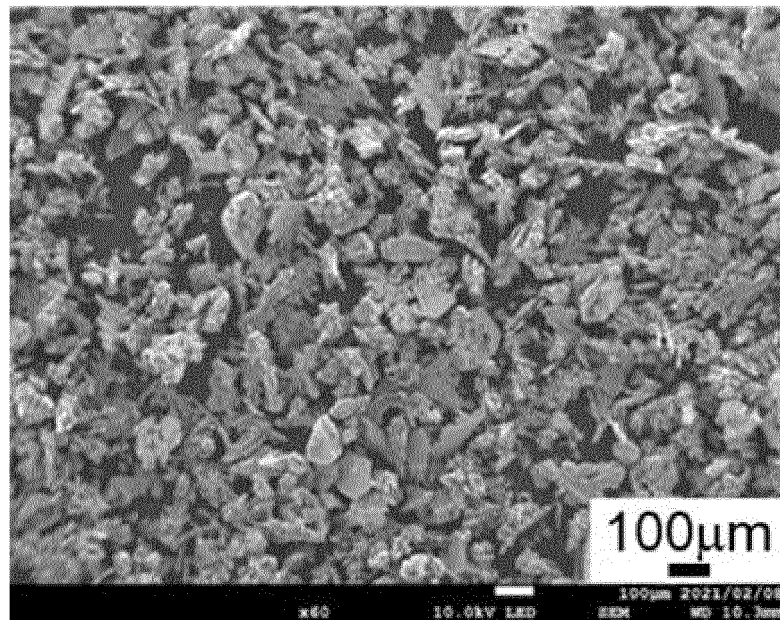
[Fig. 7]



[Fig. 8]



(A)

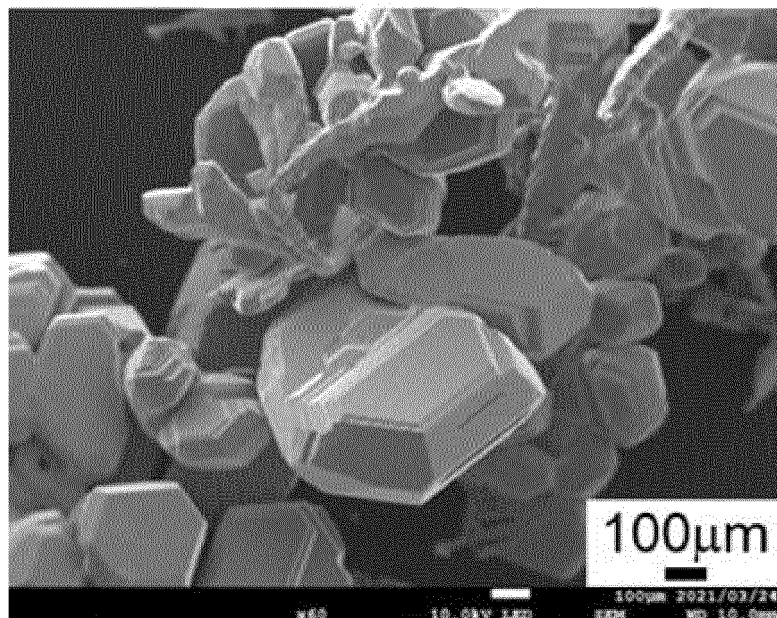


(B)

[Fig. 9]



(A)



(B)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/011426

A. CLASSIFICATION OF SUBJECT MATTER

C25C 3/28(2006.01)i; **C22B 34/12**(2006.01)i
FI: C25C3/28; C22B34/12 103

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)

C25C3/28; C22B34/12

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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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	JP 2015-507696 A (UNIVERSAL TECHNICAL RESOURCE SERVICES, INC.) 12 March 2015 (2015-03-12) claims, paragraphs [0037]-[0042], [0063]-[0069], [0086]-[0089]	1-11
Y	JP 6-173065 A (JAPAN ENERGY CORP.) 21 June 1994 (1994-06-21) paragraph [0016]	1-11
Y	WO 2018/159774 A1 (KYOTO UNIV.) 07 September 2018 (2018-09-07) paragraphs [0027]-[0034], [0085]-[0086]	1-11
A	WO 2020/044841 A1 (TOHO TITANIUM CO., LTD.) 05 March 2020 (2020-03-05) paragraph [0052]	1-11

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance
“E” earlier application or patent but published on or after the international filing date
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
“O” document referring to an oral disclosure, use, exhibition or other means
“P” document published prior to the international filing date but later than the priority date claimed

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

01 April 2022

Date of mailing of the international search report

19 April 2022

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.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2022/011426

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2015-507696 A	12 March 2015	US 2013/0164167 A1 claims, paragraphs [0102]-[0107], [0129]-[0133], [0151]-[0156] US 2018/0023208 A1 US 2018/0094357 A1 US 2020/0024761 A1 WO 2013/096893 A1 EP 2794943 A1 EP 3561091 A1 TW 201341539 A AU 2012358205 A ZA 201404758 B AU 2017279628 A	
JP 6-173065 A	21 June 1994	(Family: none)	
WO 2018/159774 A1	07 September 2018	US 2020/0385881 A1 paragraphs [0083]-[0087] CN 110366609 A KR 10-2019-0122787 A	
WO 2020/044841 A1	05 March 2020	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

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 2015507696 A [0004] [0027]