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(54) **METHOD FOR PURIFYING TITANIUM MATERIAL**

(57) This method for purifying a titanium material is a deoxidization method for removing oxygen contained in a titanium material from the titanium material that is formed from pure titanium, a titanium alloy or an inter-metallic compound that contains titanium as one of the main components. This method for purifying a titanium material comprises: a first melting step wherein hydrogen is introduced into the titanium material in a molten state by melting the titanium material in a rare gas atmosphere

containing 5-70% by volume of hydrogen; and a second melting step wherein oxygen contained in the titanium material is removed together with hydrogen from the titanium material in a molten state by melting the titanium material, into which hydrogen has been introduced during the first melting step, in a rare gas atmosphere. The first melting step and the second melting step are carried out one or more times, respectively.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method for refining a titanium material in which oxygen contained in a titanium material made of a pure titanium, a titanium alloy or an intermetallic compound containing titanium as one of main components, and further hydrogen are removed from the titanium material.

BACKGROUND ART

10 **[0002]** In recent years, demands for titanium such as pure titanium or titanium alloys have increased particularly as metal materials for transports such as airplanes or automobiles utilizing properties of titanium such as light weight, high corrosion resistance and high specific strength.

15 **[0003]** Since titanium is active, it is called active metal. Titanium is very easily combined with light elements such as oxygen, nitrogen, etc. Typically, once titanium is combined with such a light element, it is very difficult to remove the light element. Although titanium has excellent properties as described above, there is a problem that light elements combined with titanium are hardly removed. Further, there is another problem that titanium is more expensive than a steel material or an aluminum material that has been typically used. Because of those problems, currently, titanium has not been spread to the market yet.

20 **[0004]** In consideration of the current situation, recycling of titanium scraps or use of low-quality materials have been investigated many times before in order to reduce the cost and save the resources. However, the titanium scraps or the low-quality materials contain plenty of light elements. Among the light elements, oxygen contained therein (hereinafter also referred to as contained oxygen simply) forms an obstacle. Thus, such an investigation has not been put into practical use on an industrial level.

25 **[0005]** In addition, recent research and development are active on application of hearth melting for producing an ingot using a water-cooling copper mold with an electron beam or a plasma arc as a heat source, or additive manufacturing making use of powder.

[0006] Non-Patent Literature 1 or Non-Patent Literature 2 is a technical literature describing a method for removing contained oxygen from a titanium material such as a pure titanium or a titanium alloy by use of hydrogen.

30 **[0007]** Non-Patent Literature 1 describes that oxygen can be reduced by arc melting of sponge titanium or a Ti-6Al-4V alloy under an Ar atmosphere containing 1 to 30 vol% of H₂. For example, it is described that in a case where the sponge titanium is used as a material, oxygen concentration decreases from 0.04 mass% to 0.016 mass%. On the other hand, it is described that in a case where the Ti-6Al-4V alloy is used as a material, an oxygen concentration decreases from 0.12 mass% to 0.028 mass% and an oxygen concentration decreases from 1.6 mass% to 0.3 mass%.

35 **[0008]** On the other hand, Non-Patent Literature 2 describes that oxygen can be reduced by plasma arc melting of a pure titanium under an Ar atmosphere containing 20 vol% of H₂. In addition, Non-Patent Literature 2 describes that oxygen concentration decreases from initial oxygen concentration of 0.23 mass% to 0.09 mass%.

CITATION LIST

40 PATENT LITERATURE

[0009]

45 Non-Patent Literature 1: Y. Su et al., "Deoxidation of titanium alloy using hydrogen", Int. J. Hydrogen Energy, 34 (2009) 8958-8963

Non-Patent Literature 2: J. M. Oh et al., "Brief review of removal effect of hydrogen plasma arc melting on refining of pure titanium and titanium alloys", Int. J. Hydrogen Energy, 41 (2016) 23033-23041

50 SUMMARY OF INVENTION

TECHNICAL PROBLEM

55 **[0010]** Non-Patent Literature 1 describes that an ICP analysis method is used as an oxygen analysis method. However, there is no suggestion about specific experimental conditions on which the data was obtained. Typically in the ICP analysis method, it is difficult to precisely analyze oxygen concentration in a sample due to existence of oxygen atoms contained in water molecules used for producing a solution for quantitative analysis.

[0011] In addition, Non-Patent Literature 2 also shows a graph illustrating a change with time of oxygen concentration

in a sample. Considering the inclination of the illustrated graph, it is difficult to expect further effect of reducing oxygen.

[0012] The present invention has been developed in consideration of the aforementioned situation of the background art. An object of the present invention is to provide a method for refining a titanium material in which contained oxygen and further hydrogen can be surely removed from a titanium material made of a pure titanium, a titanium alloy or an intermetallic compound containing titanium as one of main components.

SOLUTION TO PROBLEM

[0013] The method for refining a titanium material according to the present invention is a method for refining a titanium material, in which oxygen contained in a titanium material made of a pure titanium, a titanium alloy or an intermetallic compound containing titanium as one of main components is removed, the method including: a first melting step of melting the titanium material under a noble gas atmosphere containing 5 to 70 vol% of hydrogen, thereby introducing hydrogen into a melt of the titanium material; and a second melting step of melting the titanium material into which hydrogen has been introduced in the first melting step under a noble gas atmosphere, thereby removing oxygen contained in the titanium material from the melt of the titanium material together with the hydrogen, in which each of the first melting step and the second melting step is carried out at least once.

[0014] In addition, the method for refining a titanium material according to the present invention preferably further includes a heat treatment step of retaining the titanium material for 15 minutes or more under the condition of a degree of vacuum of 1×10^{-2} to 1×10^{-4} Pa and a retention temperature of 600 to 1,200°C after termination of the second melting step, thereby removing hydrogen from the titanium material.

ADVANTAGEOUS EFFECTS OF INVENTION

[0015] In the method for refining a titanium material according to the present invention, contained oxygen and further hydrogen can be removed from a titanium material made of a pure titanium, a titanium alloy or an intermetallic compound containing titanium as one of main components.

DESCRIPTION OF EMBODIMENT

[0016] The present inventors conducted earnest investigations in order to find out a method for refining a titanium material in which light elements or particularly oxygen contained in a titanium material containing, as its main component, titanium, which is very likely to be combined with light elements such as oxygen, nitrogen, etc., can be surely removed from the titanium material.

[0017] As a result, it has been found that oxygen contained in the titanium material can be surely removed by performing a first melting step of melting the titanium material under a noble gas atmosphere containing a certain amount of hydrogen so as to introduce hydrogen, and successively a second melting step of melting the titanium material under a noble gas atmosphere so as to remove contained oxygen from the titanium material together with the hydrogen introduced in the first step. Thus, the present invention has been completed.

[0018] In addition, it was also confirmed that the hydrogen introduced into the titanium material in order to remove the contained oxygen can be surely removed by performing a heat treatment step of retaining the titanium material under a certain condition after the second melting step. It is considered that in a case where the heat treatment step is carried out, the hydrogen that cannot be quite removed in the second melting step can be surely removed.

[0019] It is considered that the reason why the oxygen contained in the titanium material can be removed from the titanium material together with the hydrogen introduced in the first melting step is because the introduced hydrogen functions as a deoxidizer.

[0020] The present invention will be described more in detail based on an embodiment below.

(Titanium Material)

[0021] The titanium material used in the method for refining a titanium material of the present invention contains any one of a pure titanium, a titanium alloy, and an intermetallic compound of titanium (an intermetallic compound containing titanium as one of main components). Examples of the pure titanium include commercially pure titanium of JIS titanium 1, JIS titanium 2, JIS titanium 3, and JIS titanium 4. Examples of alloy elements contained in the titanium alloy include Al, V, Mo, Cr, Zr, Sn, Si, Cu, Nb, Fe, Ni, Ta, Ag, Pd, C, and N. Examples of the intermetallic compound include TiAl and NiTi.

[0022] The titanium content of the titanium material is preferably 45 mass% or higher. The lower limit of the titanium content of a typical titanium material is such a degree. If the titanium content of a material is too low, the material cannot be regarded as a titanium material.

(Refining Method)

[0023] The method for refining titanium of the present invention includes at least a first melting step and a second melting step. Each of the first melting step and the second melting step is carried out once to several times. In addition, a heat treatment step may be carried out after termination of the second melting step. The refining method will be separated into the first melting step, the second melting step and the heat treatment step below, and each of the steps will be described in detail.

(First Melting Step)

[0024] The first melting step is a step for introducing hydrogen into the titanium material. The first melting step is a pretreatment step for removing oxygen from the titanium material. The techniques shown in previously-described Non-Patent Literature 1 and Non-Patent Literature 2 suggest that oxygen can be reduced in a case where a step corresponding to the first melting step is carried out.

[0025] However, in the present invention, oxygen cannot be removed from the titanium material only by the first melting step. As described as Comparative Examples in the chapter of EXAMPLES which will be described later, oxygen cannot be removed satisfactorily from the titanium material only by performing the first melting step.

[0026] In the first melting step, the titanium material is melted under a noble gas atmosphere containing 5 to 70 vol% of hydrogen, for example, by use of a plasma arc melting furnace, thereby introducing hydrogen into a melt of the titanium material.

[0027] The melting in the first melting step is preferably performed by plasma arc melting. In a case where the titanium material is melted by plasma arc melting, heating and hydrogen introduction can be attained concurrently as long as hydrogen is mixed into plasma gas. In a case of melting other than the plasma arc melting, an apparatus or the like for introducing hydrogen gas must be prepared separately from a heat source, and thus the manufacturing cost increases.

[0028] In addition, the reason why the noble gas atmosphere containing 5 to 70 vol% (5 vol% or higher and 70 vol% or lower) of hydrogen is used as the atmosphere in the first melting step is as follows. If the hydrogen concentration exceeds 70 vol% particularly in the case of the plasma arc melting, energy necessary for ionization increases, and arc extinguishing often occurs due to increase in voltage, so that a plasma arc is hardly generated. On the other hand, if the hydrogen concentration is less than 5 vol%, sufficient hydrogen cannot be introduced into the melt of the titanium material.

[0029] The lower limit of the hydrogen content may be preferably 10 vol% or higher, and more preferably 15 vol% or higher. On the other hand, the upper limit of the hydrogen content may be preferably 60 vol% or lower, and more preferably 50 vol% or lower.

[0030] In addition, although the noble gas atmosphere containing 5 to 70 vol% of hydrogen is used as the atmosphere in the first melting step, an Ar atmosphere can be used as the insert gas atmosphere by way of example. Further, deoxidation can be attained in principle even when the atmosphere in the first melting step is an He atmosphere, an Ne atmosphere, or the like.

[0031] Although the amount of heat inputted in the first melting step is not particularly stipulated in the present invention, it is preferably set within a range of 15 to 200 kW/kg (15 kW/kg or more and 200 kW/kg or less). If the inputted amount of heat is less than 15 kW/kg, necessary amount of heat for melting titanium cannot be secured. On the other hand, if the inputted amount of heat exceeds 200 kW/kg, a volatilization loss of titanium occurs.

[0032] In addition, although the melting retention time in the first melting step is also not particularly stipulated, it is preferably set within a range of 0.3 to 3.6 ks (5 to 60 minutes). The lower limit of the melting retention time is more preferably set at 0.6 ks (10 minutes), and the upper limit thereof is more preferably 1.8 ks (30 minutes). If the melting retention time is less than 0.3 ks (5 minutes), sufficient hydrogen for deoxidation cannot be introduced. On the other hand, if the melting retention time exceeds 3.6 ks (60 minutes), both the heat loss and the volatilization loss of titanium merely increase.

[0033] The first melting step is typically carried out only once. However, the first melting step may be carried out again after the second melting step is carried out. Further, the first melting step may be carried out successively and repeatedly two or more times. Whether the first melting step is carried out once or a plurality of times may be determined based on a criterion that the oxygen concentration has been reduced to 80% or lower in comparison with that before the treatment.

(Second Melting Step)

[0034] The second melting step is a step of removing oxygen contained in the titanium material from the melt of the titanium material together with the hydrogen introduced into the titanium material in the first melting step.

[0035] As described above, the melting in the first melting step is preferably carried out by plasma arc melting. The melting in the second melting step is also preferably carried out by plasma arc melting. In the same manner as in the

first melting step, in a case where the titanium material is melted by plasma arc melting, the temperature of the melt can be increased to be higher than by another process. In a case of melting other than the plasma arc melting, it is expected that the deoxidation efficiency is slightly lowered due to a temperature fall.

[0036] In addition, a noble gas atmosphere of Ar, He, Ne or the like is used as the atmosphere in the second melting step. For example, in a case where the atmosphere in the first melting step is set as the Ar atmosphere containing 5 to 70 vol% of hydrogen, an Ar atmosphere being the same kind of noble gas as in the first melting step is preferably used in the second melting step, in view of efficiency. However, another noble gas such as He, Ne or the like may be used as the atmosphere in the second melting step, in the same manner as in the first melting step.

[0037] In a case where a noble gas atmosphere not containing hydrogen is used in the second melting step, the oxygen contained in the titanium material can be surely removed from the melt of the titanium material together with the hydrogen introduced into the titanium material in the first melting step. Although the atmosphere is set as the noble gas atmosphere not containing hydrogen, an extremely small amount (lower than 5 vol%) of hydrogen may be contained as long as it gives no influence to the removal of hydrogen and oxygen from the melt of the titanium material.

[0038] The amount of heat inputted in the second melting step is preferably set within a range of 15 to 200 kW/kg in the same manner as in the first melting step. If the inputted amount of heat is less than 15 kW/kg, necessary amount of heat for melting titanium cannot be secured. On the other hand, if the inputted amount of heat exceeds 200 kW/kg, a volatilization loss of titanium occurs.

[0039] In addition, although the melting retention time in the second melting step is also not particularly stipulated, it is preferably set within a range of 0.3 to 3.6 ks (5 to 60 minutes) in the same manner as the melting retention time in the first melting step. The lower limit of the melting retention time is more preferably set at 0.6 ks (10 minutes), and the upper limit thereof is more preferably set at 1.8 ks (30 minutes). If the melting retention time is less than 0.3 ks (5 minutes), sufficient time for deoxidation cannot be secured. On the other hand, if the melting retention time exceeds 3.6 ks (60 minutes), both the heat loss and the volatilization loss of titanium merely increase.

[0040] The second melting step is typically carried out only once in the same manner as the first melting step. However, the second melting step may be carried out a plurality of times in the same manner as the first melting step. In a case where the second melting step is carried out a plurality of times, a combination of the first melting step and the second melting step may be regarded as one set and performed a plurality of times, or only the second melting step may be carried out a plurality of times after termination of the first melting step. Whether the second melting step is carried out only once or a plurality of times may be determined based on a criterion that the hydrogen concentration has been reduced to 5.0×10^{-2} mass% or lower.

(Heat Treatment Step)

[0041] The heat treatment step is carried out after termination of the second melting step. In the heat treatment step, the titanium material is retained for 0.9 ks (15 minutes) or more under the condition of a degree of vacuum of 1×10^{-2} to 1×10^{-4} Pa and a retention temperature of 600 to 1,200°C.

[0042] The heat treatment step does not have to be always carried out. However, in a case where the heat treatment step is carried out, the hydrogen which cannot be quite removed in the second melting step can be surely removed.

[0043] The heat treatment step is carried out by use of a vacuum heat treatment furnace or the like. On that occasion, the degree of vacuum is set within a range of 1×10^{-2} to 1×10^{-4} Pa. The reason why the upper limit of the degree of vacuum is set at 1×10^{-4} Pa is because a degree of vacuum exceeding 1×10^{-4} Pa is preferable only for the sake of dehydrogenation but it is inefficient to take a long time to exhaust the gas to the aforementioned degree of vacuum. On the other hand, the reason why the lower limit of the degree of vacuum is set at 1×10^{-2} Pa is because in a case of a degree of vacuum less than 1×10^{-2} Pa, an oxide film is formed in the titanium surface and the removal of hydrogen is impeded by the oxide film.

[0044] In addition, the retention temperature in the heat treatment step is set at 600 to 1,200°C. The reason why the lower limit of the retention temperature is set at 600°C is because if the retention temperature is lower than 600°C, the diffusion rate of hydrogen in the solid titanium material becomes so low that it takes a long time to remove hydrogen, which is inefficient. On the other hand, the reason why the upper limit of the retention temperature is set at 1,200°C is because, if the retention temperature is higher than 1,200°C, the formation of an oxide film in the titanium surface becomes active and the time required for cooling increases.

[0045] In addition, the retention time in the heat treatment step is set at 0.9 ks (15 minutes) or more. If the retention time is less than 0.9 ks (15 minutes), it is highly likely that the hydrogen which cannot be quite removed from the titanium material in the second melting step cannot be removed. In a case where the retention time is set at 0.9 ks (15 minutes) or more, the hydrogen which cannot be quite removed from the titanium material in the second melting step can be surely removed.

[0046] As the retention time is longer, the hydrogen can be removed from the titanium material more surely. However, it is considered that substantially all the hydrogen in the titanium material can be removed in the retention time of about

3.6 ks (60 minutes).

EXAMPLES

[0047] The present invention will be described more specifically along examples. Needless to say, the present invention is not limited to the following examples, but the present invention can be carried out with suitable modifications as long as the modifications can meet the gist of the present invention. Any of the modifications is included in the technical scope of the present invention.

[0048] In each example, by use of a titanium material (commercially pure titanium: melting material made of CP titanium), the first melting step and the second melting step in a plasma arc melting furnace and the heat treatment step in a vacuum heat treatment furnace were carried out sequentially in accordance with testing conditions. A hearth used for melting the titanium material was shaped into a semisphere having a diameter of 80 mm. In a case of a titanium melt mass (sample mass) being 250 g, the titanium material was put onto the hearth so as to reach a height of about 25 mm. In a case of a titanium melt mass (sample mass) being 500 g, the titanium material was put onto the hearth so as to reach a height of about 40 mm.

[0049] In addition, the melting power of a plasma arc in the first melting step was set at 70 V and 500 A, and the melting power in the second melting step was set at 50 V and 450 A. In the first melting step, the melting time was set within a range of 0.3 to 3.6 ks (5 to 60 minutes), and the flow rate was set at 30 L/min. In the second melting step, the melting time was set within a range of 0.3 to 3.6 ks (5 to 60 minutes), and the flow rate was set at 20 L/min. The amount of heat inputted in the first melting step and the second melting step was 114 kW/kg, and the furnace pressure was 1 atm.

[0050] For the test in each Example (inventive example), by use of the aforementioned titanium material as a melting material, the first melting step and the second melting step were carried out sequentially once to several times as melting steps, and the heat treatment step was carried out if necessary. On the other hand, for testing in each Comparative Example, by use of the aforementioned titanium material as a melting material, only the first melting step was carried out as a melting step, and the heat treatment step was carried out if necessary.

[0051] As the atmosphere in the first melting step, an Ar atmosphere in which 30 vol% of hydrogen had been mixed was used. As the atmosphere in the second melting step, an Ar atmosphere (pure Ar atmosphere) in which no hydrogen had been mixed was used. In addition, in the heat treatment step, a sample having been subjected to the melting steps was placed on an Al_2O_3 boat on which a Ti sheet was laid, and evacuated to 7.0×10^{-3} Pa by a vacuum pump. After that, the temperature was increased to 1,023 K (750°C) while the vacuum state (7.0×10^{-3} Pa) was retained, and then retained for a retention time of 3.6 ks (60 minutes).

[0052] In the test, samples were picked from the outermost surface of the titanium material (test piece) which had not been subjected to the test yet and the outermost surface of the test piece which had been subjected to the final step (which was either the first melting step, the second melting step or the heat treatment step depending on the testing conditions). The oxygen concentration in the sample which had not been subjected to the test yet, and the oxygen concentration and the hydrogen concentration in the sample which had been subjected to the final step were measured by a noble gas melting infrared absorbing method, and evaluated. The analysis of hydrogen was based on a half quantity system. Test results are shown in Table 1.

[Table 1]

Item	Sample mass [g]	First melting step		Second melting step		Heat treatment step	Oxygen density [mass%]		Hydrogen density [mass%]	Note
		time [min]	times	time [min]	times		before treatment	after treatment		
Comp. Example 1	250	15	1	-	-	-	0.105	0.254	6.80×10^{-1}	
Comp. Example 2	250	15	1	-	-	yes	0.105	0.107	1.89×10^{-3}	
Comp. Example 3	250	15	2	-	-	yes	0.105	0.099	2.24×10^{-3}	
Comp. Example 4	250	30	1	-	-	-	1.57	1.55	4.93×10^{-1}	
Comp. Example 5	250	30	1	-	-	yes	1.57	1.48	2.09×10^{-3}	
Example 1	250	30	1	20	1	-	0.105	0.049	1.07×10^{-2}	
Example 2	250	30	1	20	1	yes	0.105	0.059	1.84×10^{-3}	
Example 3	250	5	1	20	1	-	0.105	0.049	8.25×10^{-3}	
Example 4	250	15	1	20	1	-	0.105	0.061	1.01×10^{-2}	
Example 5	250	15	2	20	1	-	0.105	0.057	1.27×10^{-2}	sample reversed
Example 6	250	15	2	20	1	yes	0.105	0.045	7.80×10^{-4}	sample reversed
Example 7	250	30	1	20	1	-	0.105	0.021	9.28×10^{-3}	cooled gradually
Example 8	250	30	2	20	2	-	0.105	0.040	7.89×10^{-3}	sample reversed
Example 9	250	30	2	20	2	yes	0.105	0.043	2.16×10^{-3}	sample reversed
Example 10	250	5	3	10	3	-	0.105	0.077	3.52×10^{-2}	
Example 11	250	5	3	10	3	yes	0.105	0.062	1.52×10^{-3}	

(continued)

Item	Sample mass [g]	First melting step		Second melting step		Heat treatment step	Oxygen density [mass%]		Hydrogen density [mass%]	Note
		time [min]	times	time [min]	times		before treatment	after treatment		
Example 12	500	30	1	20	1	-	0.105	0.055	1.19×10^{-2}	
Example 13	500	30	1	20	1	yes	0.105	0.054	5.50×10^{-4}	
Example 14	250	30	1	20	1	-	1.57	0.709	9.00×10^{-3}	
Example 15	250	30	1	20	1	yes	1.57	0.696	7.80×10^{-4}	
Example 16	250	15	4	15	4	-	1.57	0.724	1.70×10^{-2}	sample reversed
Example 17	250	15	4	15	4	yes	1.57	0.696	4.40×10^{-4}	sample reversed
Example 18	250	15	4	15	4	-	1.57	0.725	1.87×10^{-2}	
Example 19	250	15	4	15	4	yes	1.57	0.697	7.90×10^{-4}	

[0053] In Examples 5 and 6, the sample was reversed between the first melting steps performed twice such that the first melting step, sample reversing, the first melting step ... were performed sequentially.

[0054] In Examples 8, 9, 16 and 17, the sample was reversed at the time of repeating of the series of steps such that the first melting step, the second melting step, sample reversing, the first melting step ... were performed sequentially.

[0055] The gradually cooling in Example 7 was carried out by decreasing a current value from 450 A at a rate of 50 A per 20 seconds in the second melting step, and turning off the plasma as soon as the current value reached 50 A.

[0056] It is understood that deoxidation proceeded steadily in each Example (inventive example) where the titanium material was refined under the conditions satisfying the requirements of the present invention while refining did not proceed in each Comparative Example.

[0057] From the results, it is understood that refining does not proceed satisfactorily only by the melting step (first melting step) in which the titanium material is melted under the Ar atmosphere containing 5 to 70 vol% of hydrogen so as to introduce the hydrogen into the titanium material, but refining proceeds by performing the second melting step following the first melting step such that the titanium material is melted under the Ar atmosphere not containing hydrogen.

[0058] It can be considered that the hydrogen introduced into the titanium material in the first melting step functions as a deoxidizer in the second melting step such that oxygen contained in the titanium material is removed from the titanium material together with the hydrogen.

[0059] The embodiment disclosed here should be interpreted not to be restrictive but to be exemplary in all respects. Particularly, as for items which are not disclosed clearly in the embodiment disclosed here, for example, running conditions or operating conditions, various parameters, dimensions, weights and volumes of constituents, etc., values which can be assumed easily by a person skilled in the art without departing from the range performed regularly by a person skilled in the art are employed.

[0060] The present application is based on Japanese patent application No. 2017-210129 filed on October 31, 2017, the contents of which are incorporated herein by reference.

INDUSTRIAL APPLICABILITY

[0061] According to the present invention, recycling of titanium scraps or use of low-quality materials can be attained.

Claims

1. A method for refining a titanium material, in which oxygen contained in a titanium material made of a pure titanium, a titanium alloy or an intermetallic compound containing titanium as one of main components is removed, the method comprising:

a first melting step of melting the titanium material under a noble gas atmosphere containing 5 to 70 vol% of hydrogen, thereby introducing hydrogen into a melt of the titanium material; and
a second melting step of melting the titanium material into which hydrogen has been introduced in the first melting step under a noble gas atmosphere, thereby removing oxygen contained in the titanium material from the melt of the titanium material together with the hydrogen,
wherein each of the first melting step and the second melting step is carried out at least once.

2. The method for refining a titanium material according to claim 1, further comprising a heat treatment step of retaining the titanium material for 15 minutes or more under the condition of a degree of vacuum of 1×10^{-2} to 1×10^{-4} Pa and a retention temperature of 600 to 1,200°C after termination of the second melting step, thereby removing hydrogen from the titanium material.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/040049

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22B34/12 (2006.01) i, C22B7/00 (2006.01) i, C22B9/04 (2006.01) i,
C22B9/05 (2006.01) i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C22B34/12, C22B7/00, C22B9/04, C22B9/05, B22F9/22

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 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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

JSTPlus/JMEDPlus/JST7580 (JDreamIII) & キーワード: チタンおよび Ti、水素、脱酸、成島尚之

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SU, Yanqing, WANG, Liang, LUO, Liangshun, JIANG, Xiaohong, GUO, Jingjie, FU, Hengzhi, International Journal of HYDROGEN ENERGY, vol. 34 no. 21, ScienceDirect, November 2009, ISSN: 0360-3199, pp. 8958-8963	1-2
A	OH, Jung-Min, ROH, Ki-Min, LIM, Jae-Won, International Journal of HYDROGEN ENERGY, vol. 41 no. 48, ScienceDirect, 28 December 2016, ISSN:0360-3199, pp. 23033-23041	1-2



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search
17 December 2018 (17.12.2018)

Date of mailing of the international search report
25 December 2018 (25.12.2018)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/040049

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-1435481 B1 (KOREA INSTITUTE OF GEO SCIENCE AND MINERAL RESOURCES) 22 August 2014, entire text, all drawings (Family: none)	1-2
A	CN 102517464 A (NO.52 INSTITUTE OF CHINA NORTH INDUSTRIES GROUP CORPORATION) 27 June 2012, entire text, all drawings (Family: none)	1-2
A	US 2016/0177418 A1 (KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY) 23 June 2016, entire text, all drawings & WO 2014/148687 A1 & KR 10-1370029 B1	1-2
A	KR 10-2013-0010742 A (KOREA INSTITUTE OF GEOSCIENCE AND MINERAL RESOURCES) 29 January 2013, entire text, all drawings (Family: none)	1-2
A	US 2009/0107290 A1 (LOS ALAMOS NATIONAL SECURITY, LLC) 30 April 2009, entire text, all drawings (Family: none)	1-2

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2017210129 A [0060]

Non-patent literature cited in the description

- **Y. SU et al.** Deoxidation of titanium alloy using hydrogen. *Int. J. Hydrogen Energy*, 2009, vol. 34, 8958-8963 [0009]
- **J. M. OH et al.** Brief review of removal effect of hydrogen plasma arc melting on refining of pure titanium and titanium alloys. *Int. J. Hydrogen Energy*, 2016, vol. 41, 23033-23041 [0009]