

Specification

[Title of the Invention] TITANIUM MATERIAL AND METHOD FOR
MANUFACTURING TITANIUM MATERIAL

[Technical Field of the Invention]

[0001]

The present invention relates to a titanium material and a method for manufacturing a titanium material. Priority is claimed on Japanese Patent Application No. 2020-155144, filed in Japan on September 16, 2020, the content of which is incorporated herein by reference.

[Background Art]

[0002]

Titanium materials that are used as building materials for walls, roofs or the like of buildings (titanium materials for building materials) are roughly classified into non-colored materials exhibiting silvery color that is the color of titanium itself and colored materials that are given an oxide film having a certain thickness on the surface by anode oxidation, thereby exhibiting interference color such as red or blue and having designability.

[0003]

Due to the excellent corrosion resistance, titanium materials are also in use as a building material in seaside areas where salt adheres to titanium materials. Twenty years or more have passed since titanium materials began to be used as building materials, but there have been thus far no reports of corrosion that is considered as a problem. Both non-colored materials and colored materials exhibit excellent corrosion resistance.

[0004]

There are cases where discoloration occurs when both non-colored materials and colored materials are exposed to the atmosphere or the like for a long period of time. It has been clarified that this discoloration is interference color that is generated by an increase in the thickness of an oxide film on the surface of a titanium material up to approximately several tens of nanometers due to an acidic environment with a pH of 4.5 or less, for example, acid rain or the like. Such an oxide film having a thickness of several tens of nanometers does not impair the corrosion resistance of titanium. However, in portions such as the walls or roofs of buildings where external appearance is important, there is a demand for titanium materials where the generation of interference color due to an increase in the thickness of an oxide film is less likely to occur, in particular, non-colored materials, and development of such titanium materials is underway.

[0005]

For example, Patent Document 1 discloses a titanium material that is less likely to discolor in the atmospheric environment, in which the average carbon concentration in a range from the outermost surface to a depth of 100 nm is 14 atom% or less, and an oxide film having a thickness of 12 to 40 nm is present on the outermost surface.

[0006]

Patent Document 2 discloses a titanium material that is less likely to discolor, in which the fluorine content in an oxide film on the surface is 7 atom% or less.

[0007]

Patent Document 3 discloses a titanium material that is less likely to discolor in the atmospheric environment, in which, in an oxide membrane formed on the titanium surface, in the oxide membrane that is present in a 3 nm range from the titanium surface, in a case where the composition of titanium oxide is indicated by TiO_x , x is

within a range of 0.8 to 1.8, and the density of the oxide membrane is 4.2 g/cm³ or more. The titanium material disclosed in Patent Document 3 is manufactured by a method or the like in which a titanium surface is treated with a mixed solution of nitric acid and hydrofluoric acid and then treated with a nitric acid solution.

[0008]

Patent Document 4 discloses a pure titanium material for building materials that is used as a building material, in which, as impurity elements, Fe is suppressed to 0.08 mass% or less, Nb is suppressed to 0.02 mass% or less, and Co is suppressed to 0.02 mass% or less. The titanium material disclosed in Patent Document 4 is manufactured by carrying out heating for a predetermined time at 130°C to 280°C in the atmosphere or in a vacuum following pickling in the final step.

[Prior Art Document]

[Patent Document]

[0009]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2002-12962

[Patent Document 2] Japanese Unexamined Patent Application, First Publication No. 2002-47589

[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. 2005-154882

[Patent Document 4] Japanese Unexamined Patent Application, First Publication No. 2004-300569

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0010]

Non-colored materials are required to have high weather resistance by which interference color is not generated. Furthermore, in recent years, there has been a demand for a titanium material that is less likely to discolor in spite of an increase in temperature due to changes in the atmospheric environment and even in an acidic environment having a pH of 3.0 or less, which is even more severe than what has been described above.

[0011]

In Patent Documents 1 to 4, weather resistance is evaluated as described below. The titanium material is immersed in a sulfuric acid aqueous solution having a pH of 3 to 4 at 60°C for several days, and the weather resistance is evaluated with the color difference before and after the immersion. In addition, it is described that the color difference is 3 to 7 when the titanium material is immersed in a sulfuric acid aqueous solution having a pH of 3 at 60°C for 7 days or 14 days and the color difference is less than 5, furthermore, less than 1 when the titanium material is immersed in a sulfuric acid aqueous solution having a pH of 4 at 60°C for 3 days. However, in the above-described weather resistance evaluation, it is not possible to sufficiently reflect the use in high-temperature environments. In addition, in a case where the titanium materials described in Patent Documents 1 to 4 are immersed in a sulfuric acid aqueous solution having a pH of 4 at 80°C for 4 days, the color differences before and after the immersion are about 15 or more, and conventional titanium materials do not have sufficient weather resistance under higher temperature conditions.

[0012]

That is, it has been difficult for conventional titanium materials to realize weather resistance in severe acidic environments.

[0013]

The present invention has been made in view of the above problems, and an object of the present invention is to provide a titanium material having excellent weather resistance and a method for efficiently manufacturing the titanium material.

[Means for Solving the Problem]

[0014]

As a result of detailed studies of the relationship between surface oxide films that are formed on titanium materials and weather resistance, the present inventors found that, in a case where a specific element is contained in the surface oxide films, the weather resistance is excellent. In addition, the present inventors found that the element content of the surface oxide film can be controlled by a cleaning step in which nitric hydrofluoric acid is used. Furthermore, it was newly found that weather resistance in acidic environments can be obtained by carrying out the above-described cleaning step in the final step. The present inventors carried out additional studies based on the obtained knowledge and consequently attained the present invention.

[0015]

The gist of the present invention completed based on the above-described findings is as described below.

[1] A titanium material according to one aspect of the present invention, in which, when a chemical composition of a surface is analyzed by X-ray photoelectron spectroscopy, the titanium material contains, as a composition of the surface, Zn: 0.1 atom% or more and Ca: 0.5 atom% or more, and the titanium material contains, as a composition of a surface oxide film, C: 20.0 atom% or less and F: 5.0 atom% or less.

[2] In the titanium material according to [1], the surface oxide film may have a thickness of 5 to 20 nm.

[0016]

[3] In addition, a method for manufacturing a titanium material according to another aspect of the present invention having a cleaning step of cleaning a titanium raw material, in which the cleaning step includes an immersion treatment of immersing the titanium raw material in an aqueous solution having a temperature of 40°C to 60°C for 1.0 minutes or longer, where the aqueous solution contains a zinc salt: 0.00030 to 0.65000 mass% in terms of Zn, a calcium salt: 0.00060 to 0.40000 mass% in terms of Ca, HF: 1.0 to 6.0 mass%, and HNO₃: 4.0 to 10.0 mass% and a water washing treatment of washing the titanium raw material lifted from the aqueous solution with water.

[4] In the method for manufacturing a titanium material according to [3], the zinc salt may be 0.00030 to 0.00100 mass% in terms of Zn, and the calcium salt may be 0.00060 to 0.00108 mass% in terms of Ca.

[5] In the method for manufacturing a titanium material according to [3] or [4], the zinc salt may be ZnCl₂.

[6] In the method for manufacturing a titanium material according to [3] or [4], the calcium salt may be CaCl₂.

[7] In the method for manufacturing a titanium material according to [5], the calcium salt may be CaCl₂.

[8] The method for manufacturing a titanium material according to [3] or [4] may further have a heating step of heating the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere.

[9] The method for manufacturing a titanium material according to [5] may further have a heating step of heating the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere.

[10] The method for manufacturing a titanium material according to [6] may further have a heating step of heating the titanium raw material after the cleaning step to

300°C to 900°C in an inert atmosphere.

[11] The method for manufacturing a titanium material according to [7] may further have a heating step of heating the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere.

[Effects of the Invention]

[0017]

As described above, according to the present invention, it becomes possible to provide a titanium material having excellent weather resistance and a method for efficiently manufacturing the titanium material.

[Embodiments of the Invention]

[0018]

Hereinafter, a preferable embodiment of the present invention will be described in detail. The description will be carried out in the following order.

<1. Titanium material>

<2. Method for manufacturing titanium material>

[0019]

Numerical limiting ranges expressed below using “to” include the lower limit and the upper limit in the ranges. Numerical values expressed with “more than” and “less than” are not included in numerical ranges.

[0020]

<1. Titanium material>

A titanium material according to the present embodiment includes a titanium bulk material (titanium substrate) and a surface oxide film disposed on the surface of the titanium bulk material. The titanium material according to the present embodiment will be described in detail below.

[0021]

The titanium bulk material in the titanium material of the present embodiment is made of any of pure titanium or a titanium alloy. The titanium bulk material is, for example, pure titanium or a titanium alloy having a Ti content of 70 mass% or more.

[0022]

Examples of the pure titanium include commercially pure titanium defined by Classes 1 to 4 of JIS standards and Grades 1 to 4 of ASTM standards, which correspond to Classes 1 to 4 of JIS standards. That is, commercially pure titanium that is a subject of the present embodiment contains, by mass%, C: 0.1% or less, H: 0.015% or less, O: 0.4% or less, N: 0.07% or less, Fe: 0.5% or less, and a remainder including Ti and impurities. For buildings, commercially pure titanium defined by JIS Class 1 or ASTM Gr. 1, which is equivalent to JIS Class 1, or equivalent materials thereof are mainly used.

[0023]

Examples of the titanium alloy include α -type titanium alloys, $\alpha+\beta$ -type titanium alloys, and β -type titanium alloys.

[0024]

Examples of the α -type titanium alloys include highly corrosion-resistant alloys (titanium alloys defined by Classes 11 to 13, 17, and 19 to 22 of JIS standards and Grades 7, 11, 13, 14, 17, 30, and 31 of ASTM standards or titanium alloys further containing a small amount of a variety of elements), Ti-0.5Cu, Ti-1.0Cu, Ti-1.0Cu-0.5Nb, Ti-1.0Cu-1.0Sn-0.3Si-0.25Nb, Ti-0.05 to 0.2Pd, and the like.

[0025]

Examples of the $\alpha+\beta$ type titanium alloys include Ti-3Al-2.5V, Ti-5Al-1Fe, Ti-6Al-4V, and the like.

[0026]

Examples of the β -type titanium alloys include Ti-11.5Mo-6Zr-4.5Sn, Ti-8V-3Al-6Cr-4Mo-4Zr, Ti-13V-11Cr-3Al, Ti-15V-3Al-3Cr-3Sn, Ti-20V-4Al-1Sn, Ti-22V-4Al, and the like.

[0027]

In the titanium material according to the present embodiment, when the chemical composition of the surface of the titanium material is analyzed by X-ray photoelectron spectroscopy, the composition of the surface is Zn: 0.1 atom% or more and Ca: 0.5 atom% or more, and the titanium material contains, as the composition of a surface oxide film, C: 20.0 atom% or less and F: 5.0 atom% or less.

[0028]

[When the chemical composition of the surface is analyzed by X-ray photoelectron spectroscopy, the composition of the surface is Zn: 0.1 atom% or more and Ca: 0.5 atom% or more]

In the titanium material according to the present embodiment, when the chemical composition of the surface of the titanium material is analyzed by X-ray photoelectron spectroscopy, the Zn content on the surface is 0.1 atom% or more, and the Ca content is 0.5 atom% or more. Zn and Ca on the surface of the titanium material improve the weather resistance of the titanium material. The mechanism is not necessarily clear, but the present inventors assume that the improvement is attributed to any or a plurality of the inhibitor effect, oxygen deficiency repair effect, and bipolar film effect of Zn and Ca. The inhibitor effect is an effect of suppressing the growth of a surface oxide film by Zn and Ca on the surface of the titanium material preferentially dissolving in an acid rain environment to suppress the dissolution of titanium. The oxygen deficiency repair effect is an effect of suppressing the growth of the surface

oxide film by the fact that the Ti^{4+} sites in TiO_2 that configures the surface oxide film are doped with Zn^{2+} and Ca^{2+} , whereby oxygen deficiencies are repaired and, consequently, the elution of titanium is suppressed. The bipolar film effect is an effect of suppressing the growth of the surface oxide film by the fact that oxides (ZnO and CaO) having different semiconducting properties from TiO_2 are precipitated, and the migration of electrons from an acidic solution adhering to the surface of the surface oxide film is hindered.

When the chemical composition of the surface of the titanium material is analyzed by X-ray photoelectron spectroscopy, if the Zn content on the surface of the titanium material is 0.1 atom% or more, and the Ca content is 0.5 atom% or more, the weather resistance of the titanium material improves due to any or a plurality of the above-described effects. The Zn content is preferably 0.1 atom% or more or 0.2 atom% or more and more preferably 0.3 atom% or more. The Ca content is preferably 0.5 atom% or more or 0.6 atom% or more and more preferably 0.7 atom% or more. Furthermore, it is preferable that the Zn content is 1.0 atom% or less and the Ca content is 1.5 atom% or less, when the Zn content and the Ca content become higher than these values, the above-described effects tend to be saturated. The Zn content is more preferably 0.9 atom% or less. The Ca content is more preferably 1.4 atom% or less and still more preferably 1.3 atom% or less.

[0029]

[C: 20.0 atom% or less, F: 5.0 atom% or less]

The C content and the F content in the surface oxide film are 20.0 atom% or less and 5.0 atom% or less. When the C content and the F content of the surface oxide film are large, discoloration is likely to occur. This is because the surface oxide film grows due to the fact that carbon, fluorine, or a compound thereof degrades the action of

the surface oxide film that suppresses the elution of the titanium substrate, which makes it easy for titanium to be eluted or the fact that carbon or fluorine is present as a compound with titanium in the surface oxide film and the compound is likely to dissolve. Here, carbon and fluorine in the surface oxide film may be present independently or may be present as a compound with titanium, hydrogen, oxygen, or the like. When the C content is 20.0 atom% or less and the F content is 5.0 atom% or less, the elution of titanium and the growth of the surface oxide film in the titanium material are suppressed. The C content is preferably 18.0 atom% or less, 15.0 atom% or less, or 6.0 atom% or less. The F content is 4.9 atom% or less, 4.8 atom% or less, 4.5 atom% or less, or 4.0 atom% or less.

The C content and the F content of the surface oxide film are as small as possible; however, substantially, the C content is 0.5 atom% or more, and the F content is 1.0 atom% or more in terms of production. C atoms are more preferably 1.0 atom% or more. The F content is more preferably 2.0 atom% or more.

[0030]

[Thickness of surface oxide film: 5 to 20 nm]

The thickness of the surface oxide film can be set to, for example, 100 nm or less and is more preferably 80 nm or less and still more preferably 5 nm or more and 20 nm or less. When the thickness of the surface oxide film is 20 nm or less, it is possible to suppress the generation of interference color by the surface oxide film. The thickness of the surface oxide film is more preferably 18 nm or less and still more preferably 12 nm or less.

On the other hand, the thickness of the surface oxide film is preferably 5 nm or more. When the thickness of the surface oxide film is 5 nm or more, the elution of Ti that is contained in the titanium material is suppressed, and higher weather resistance

can be obtained. The thickness of the surface oxide film is more preferably 6 nm or more.

In addition, here, the thickness of the surface oxide film refers to a range from the surface of the surface oxide film to a position where the oxygen concentration becomes the intermediate concentration between the maximum concentration and the base concentration. The base concentration refers to the average oxygen concentration in a range where the oxygen concentration curve becomes flat in a range where the oxygen concentration is 5 atom% or less after XPS analysis is carried out in the depth direction from the surface of the titanium material while carrying out sputtering. “Flat” mentioned herein refers to a place where the absolute value of the slope of an approximated straight line is 0.002 or less in an arbitrary depth range including a maximum of 5 or more quantitative values of the oxygen concentration that are measured by XPS analysis to be described below. The formula of the approximated straight line is calculated by the least-square method.

[0031]

The Zn content, the Ca content, the F content and the C content of the surface oxide film, and the thickness of the surface oxide film can be obtained from the composition distribution in the depth direction from the surface obtained by XPS carried out on the titanium material that has been immersed in acetone and cleaned with ultrasonic waves. The ultrasonic cleaning time may be, for example, 30 seconds or longer. In the measurement of the Zn content and the Ca content, after the existing elements are specified by qualitative analysis through XPS, the quantitative analysis value of each element is obtained, and the Zn content and the Ca content are determined. The Zn content and the Ca content mentioned herein refer to the contents of the individual elements within a range from the surface of a sample to a depth of 8

nm or less in a state where sputtering is not carried out. As the composition analysis in the depth direction, quantitative analysis of each element is carried out every 2 nm of sputtering depth in terms of SiO₂, and the F content, the C content, and the O content are obtained from the surface of the titanium material to a depth at which the oxygen concentration reaches the base concentration. The thickness of the surface oxide film is a value obtained by multiplying the sputtering rate in terms of SiO₂ by the sputtering time, and the sputtering time is obtained at a position where the O content is halved with respect to the maximum value after XPS analysis is carried out until a depth where a baseline where the oxygen concentration curve becomes flat in a range where the oxygen concentration is 5 atom% or less. The sputtering rate in terms of SiO₂ is the sputtering rate obtained under the same measurement conditions using a SiO₂ film the thickness of which has been measured in advance using an ellipsometer. Usually, the baseline can be obtained by carrying out analysis from the surface to a position of 50 nm, but there are cases where the baseline can be obtained by carrying out analysis from the surface to a position of 100 nm depending on the surface state of the titanium material.

[0032]

The maximum fluorine concentration in the surface oxide film measured by the above-described method is regarded as the F content in the surface oxide film. In addition, since there are cases where the surface of the titanium material is affected by the adhesion of an organic substance, for carbon the concentration of which decreases almost monotonously in the depth direction, a portion where the oxygen concentration decreases near the surface of the titanium material is considered to be attributed to the influence of the adhesion of an organic substance, and, in the surface oxide film, the maximum value of the carbon concentration at the depth where the oxygen

concentration is maximized or deeper is regarded as the C content.

[0033]

The shape of the titanium material according to the present embodiment is not particularly limited and is a plate, a coil, a strip, or the like. Hitherto, the titanium material according to the present embodiment has been described.

[0034]

[Whiteness]

In recent years, from the viewpoint of designability, among non-colored materials, materials having high whiteness are in demand. As a method for efficiently obtaining a titanium material having a surface with high whiteness, a pickled surface such as nitric hydrofluoric acid pickling, for which nitric hydrofluoric acid is used, is an exemplary example. It is considered that pickling forms fine irregularities on the surface of titanium, these fine irregularities cause irregular reflection, and the whiteness of the titanium material increases. In order to obtain high whiteness, it is necessary to manufacture products using a titanium material having a pickled surface without carrying out rolling or a heat treatment after pickling. However, when exposed to the atmospheric environment for a long period of time, there are cases where the titanium material having a pickled surface discolors. This is considered to be because an oxide film that is formed after pickling includes a large number of oxygen deficiencies and thus the elution of Ti ions in the atmospheric environment cannot be prevented.

[0035]

That is, in the above-described ordinary pickled surface, whiteness can be increased, but discoloration in acidic environments becomes apparent. Therefore, it has been difficult for conventional titanium materials to realize both weather resistance in severe acidic environments and whiteness.

[0036]

The present inventors found that a titanium material satisfying both weather resistance in acidic environments and whiteness can be provided by carrying out a cleaning step including the immersion treatment using nitric hydrofluoric acid in the final step.

[0037]

Furthermore, the titanium material preferably has a whiteness L^* of 70 or higher on the surface. This makes it possible to satisfy both weather resistance and high whiteness, which is desirable from the viewpoint of designability. However, in a case where the whiteness is too high, fine surface irregularities are excessively formed, which makes sea salt particles or contaminant particles to adhere to the titanium material, increases the possibility of the particles acting as the starting point of corrosion, and also increases the possibility of the corrosion resistance deteriorating. Therefore, L^* is preferably 90 or lower. L^* is more preferably 80 or lower. A cleaning step to be described below makes it easy to achieve this whiteness.

[0038]

The whiteness is measured by, for example, the following method. That is, L^* is measured in accordance with JIS Z 8730:2009 with a light source C using a color difference meter CR-200b manufactured by Konica Minolta Japan Inc., and the whiteness is evaluated.

[0039]

<2. Method for manufacturing titanium material>

In a method for manufacturing a titanium material according to the present embodiment, a cleaning step is carried out as the final step in the manufacturing step of the titanium material. In the method for manufacturing a titanium material according

to the present embodiment, for example, an ingot step, a hot rolling step, a cold rolling step, an annealing step, and a temper rolling/stretch straightening step are sequentially carried out, and then a cleaning step is carried out. In addition, for example, the cleaning step is carried out after the annealing step in a case where the temper rolling/stretch straightening step is skipped. The above-described steps other than the cleaning step can be carried out by well-known methods.

[0040]

For example, in the ingot step, sponge titanium, a mother alloy for adding an alloying element, or the like is used as a raw material, and an ingot of pure titanium or a titanium alloy having the above-described components is produced by a variety of melting methods such as hearth melting methods such as a vacuum arc melting method, an electron beam melting method, and a plasma melting method. Next, the obtained ingot is bloomed and hot-forged as necessary to produce an ingot.

[0041]

In the hot rolling step, for example, the ingot may be heated to 600°C to 850°C and rolled at a temperature of the transformation point or lower. The rolling reduction may be determined depending on the properties of a final product. The heating temperature is preferably 700°C to 850°C. The heating temperature is preferably 700°C or higher from the viewpoint of deformation resistance. The heating temperature is preferably 850°C or lower since the thickness of an oxide film on the titanium raw material after hot rolling can be reduced and it becomes possible to carry out descaling after hot rolling under mild conditions.

[0042]

In the cold rolling step, the titanium raw material after the hot rolling needs to be rolled under conditions where desired thickness or properties can be obtained. In a

case where a plurality of times of cold rolling passes are carried out, the titanium raw material may be annealed between the cold rolling passes.

[0043]

In the annealing step after the cold rolling step, for example, this titanium raw material may be annealed in an inert atmosphere after removing impurities such as a lubricating oil adhering in the cold rolling step in an alkali cleaning line. In addition, for example, atmospheric annealing, salt bath descaling, and pickling may be sequentially carried out on the titanium raw material after the cold rolling step.

[0044]

The temper rolling/stretch straightening step may be appropriately carried out for the purpose of, for example, straightening the shape of the titanium raw material after the annealing step.

[0045]

In the cleaning step, an immersion treatment of immersing the titanium raw material in an aqueous solution having a temperature of 40°C to 60°C for 1.0 minutes or longer, where the aqueous solution contains a zinc salt: 0.00030 to 0.65000 mass% in terms of Zn, a calcium salt: 0.00060 to 0.40000 mass% in terms of Ca, HF: 1.0 to 6.0 mass%, and HNO₃: 4.0 to 10.0 mass% and a water washing treatment of washing the titanium raw material lifted from the aqueous solution with water are included.

[0046]

More preferably, in the cleaning step, an immersion treatment of immersing the titanium raw material in an aqueous solution having a temperature of 40°C to 60°C for 1.0 minutes or longer, where the aqueous solution contains a zinc salt: 0.00030 to 0.00100 mass% in terms of Zn, a calcium salt: 0.00060 to 0.00108 mass% in terms of Ca, HF: 1.0 to 6.0 mass%, and HNO₃: 4.0 to 10.0 mass% and a water washing treatment

of washing the titanium raw material lifted from the aqueous solution with water are included.

[0047]

The aqueous solution that is used in the immersion treatment contains 0.00030 to 0.65000 mass% of a zinc salt in terms of Zn. Examples of the zinc salt include ZnCl_2 , ZnSO_4 , $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}_3(\text{PO}_4)_2$, and ZnCO_3 . Among these, ZnCl_2 is preferable since the solubility in water is the highest.

[0048]

The zinc salt content is 0.00030 to 0.65000 mass% in terms of Zn. When the zinc salt content is less than 0.00030 mass% in terms of Zn, zinc oxide is not formed on the surface of the titanium material, which is the final product, to an extent that the growth of the surface oxide film can be suppressed. Therefore, the weather resistance becomes poor.

From the viewpoint of the solubility of the zinc salt and the stable manufacturing of the surface oxide film, the zinc salt content is 0.65000 mass% or less in terms of Zn.

The zinc salt content is preferably 0.00150 mass% or less in terms of Zn; however, when the zinc salt content is more than 0.00100 mass% in terms of Zn, the weather resistance is favorable, but there are cases where zinc oxide formed in the surface oxide film aggregates. Since the aggregated zinc oxide makes the surface of the titanium material nonuniform, color unevenness is caused on the surface of the titanium material, designability becomes a problem, and there are cases where the titanium material cannot be used as building materials. When the zinc salt content is 0.00100 mass% or less in terms of Zn, it is possible to suppress color unevenness. Therefore, the zinc salt content is more preferably 0.00100 mass% or less or 0.00080

mass% or less in terms of Zn. The zinc salt content is preferably 0.00060 mass% or more in terms of Zn.

[0049]

The aqueous solution that is used in the immersion treatment contains 0.00060 to 0.40000 mass% of a calcium salt in terms of Ca. Examples of the calcium salt include CaCl_2 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$, and CaCO_3 . Among these, CaCl_2 is preferable since the solubility in water is high and the deliquescency is low.

[0050]

The calcium salt content is 0.00060 to 0.40000 mass% in terms of Ca. When the calcium salt content is less than 0.00060 mass% in terms of Ca, calcium oxide is not formed on the surface of the titanium material, which is the final product, to an extent that the growth of the surface oxide film can be suppressed. Therefore, the weather resistance becomes poor.

On the other hand, from the viewpoint of the solubility of the calcium salt and the stable manufacturing of the surface oxide film, the calcium salt content is 0.40000 mass% or less. The calcium salt content may be 0.00200 mass% or less in terms of Ca. In addition, when the calcium salt content is more than 0.00108 mass% in terms of Ca, similar to the zinc oxide, there are cases where calcium oxide aggregates. Since the aggregated calcium oxide makes the surface of the titanium material nonuniform, color unevenness is caused on the surface of the titanium material, and there are cases where designability becomes a problem. When the calcium salt content is 0.00108 mass% or less in terms of Ca, it is possible to suppress color unevenness. Therefore, the calcium salt content is preferably 0.00108 mass% or less and more preferably 0.00100 mass% or less in terms of Ca. In addition, the calcium salt content is preferably 0.00072 mass% or more in terms of Ca. In a region where the aggregated

zinc oxide and calcium oxide are present on the surface of the titanium material, the O concentration is detected to be high by XPS. Therefore, in a case where the zinc oxide and the calcium oxide aggregate, the value of the thickness of the surface oxide film obtained by the above-described method becomes large.

[0051]

The aqueous solution that is used in the immersion treatment contains HF: 1.0 to 6.0 mass% and HNO₃: 4.0 to 10.0 mass%. When the aqueous solution that is used in the cleaning step contains HF: 1.0 to 6.0 mass% and HNO₃: 4.0 to 10.0 mass%, fine irregularities are formed on the surface of the titanium material. The HF content is preferably 5.0 mass% or less. The HNO₃ content is preferably 8.0 mass% or less. In addition, the HF content is preferably 1.5 mass% or more. The HNO₃ content is preferably at least 4.5 mass% or more.

[0052]

The temperature of the aqueous solution is 40°C to 60°C. When the temperature of the aqueous solution is lower than 40°C, there are cases where the titanium material is unevenly pickled and the color becomes uneven on the surface of the titanium material. On the other hand, when the temperature of the aqueous solution is higher than 60°C, fumes of HNO₃ are generated, and manufacturing facilities are adversely affected. Therefore, the temperature of the aqueous solution is 40°C to 60°C. The temperature of the aqueous solution is preferably 50°C or lower.

[0053]

The immersion time is 1.0 minutes or longer. When the immersion time is 1.0 minutes or longer, the color is uniform and fine irregularities are formed on the surface of the titanium material. On the other hand, the upper limit of the immersion time is not particularly limited, but is preferably 2.0 minutes. When the immersion time is 2.0

minutes or shorter, it is possible to carry out the treatment while maintaining the productivity of the continuous line.

[0054]

The immersion treatment makes Zn^{2+} and Ca^{2+} in the aqueous solution adsorbed onto the surface of the titanium raw material.

[0055]

After the immersion treatment, the titanium raw material is washed with water. The water washing method is not particularly limited, and the titanium raw material may be washed with water using immersion in a water washing bath, spray washing, or the like. Water washing removes the excess aqueous solution on the surface of the titanium raw material and makes a surface oxide film formed on the surface of the titanium material. At this time, oxides of Zn^{2+} and Ca^{2+} adsorbed onto the surface of the titanium raw material are formed.

[0056]

After the cleaning step, the titanium material according to the present embodiment is manufactured; however, in order to further reduce the F content of the surface oxide film, the titanium raw material after the cleaning step is preferably heated at 300°C to 900°C in an inert atmosphere as necessary. The heating of the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere makes it possible to decompose fluorotitanic acid ions that have been incorporated into the surface oxide film by heating, discharge F to the outside of the surface oxide film, and reduce the F content in the surface oxide film. The inert atmosphere is, for example, a vacuum atmosphere, an argon atmosphere, a helium atmosphere, or the like.

[0057]

The vacuum atmosphere mentioned herein refers to an atmosphere having a

degree of vacuum of 7.0×10^{-4} to 2.5×10^{-2} Pa. In addition, the argon atmosphere refers to an atmosphere containing 90 vol% or more of argon, and the helium atmosphere refers to an atmosphere containing 90 vol% or more of helium.

[0058]

The heating time is preferably 0.5 to 10.0 (hours). When the heating time is within the above-described range, fluorotitanic acid in the surface oxide film that has been incorporated during the immersion treatment is sufficiently decomposed. The lower limit of the heating time is more preferably 1.0 hour, and the upper limit of the heating time is more preferably 5.0 hours.

[0059]

An example of the results of the qualitative analysis and quantitative analysis on the surface of the titanium material by XPS for the titanium material manufactured after the cleaning step will be shown. Table 1 is an example of the quantitative analysis results by XPS of the surface of the titanium material according to the present embodiment and an example of the quantitative analysis results by XPS of the surface of an ordinary titanium material. “-” in Table 1 indicates that the value was the detection limit or less.

[0060]

[Table 1]

Element	Present invention material	Conventional material
Ca (atom%)	0.7	0.2
Zn (atom%)	0.3	-

[0061]

As shown in Table 1, in the titanium material according to the present embodiment, the Zn content was 0.3 atom%, the Ca content was 0.7 atom%, and both contents increased compared with those of the conventional materials.

Hitherto, the method for manufacturing a titanium material according to the present embodiment has been described.

[Examples]

[0062]

Hereinafter, the embodiment of the present invention will be specifically described while showing examples. The examples to be shown below are merely examples of the present invention, and the present invention is not limited to the following examples.

[0063]

(Example 1)

Titanium cold-rolled sheets (titanium substrates) of types shown in Table 2 were manufactured, a plurality of samples having a variety of sizes were cut out from each of these cold-rolled sheets, and an immersion treatment was carried out under conditions shown in Table 2. Table 2 shows the immersion treatment conditions. Subsequently, the cold-rolled sheets after the immersion treatment were washed with water by the following method. That is, the cold-rolled sheets after the immersion treatment were immersed in a water washing bath at room temperature (25°C) for 1

minute, thereby removing a pickling liquid on the surfaces.

No. 1 in Table 2 is an example in which a cleaning step was not carried out (an example of a sheet as cold-rolled and annealed), and No. 2 is an example in which a zinc salt and a calcium salt were not contained in an aqueous solution that was used in the immersion treatment in the cleaning step. CP1 shown in the item of the titanium raw material type in Table 2 indicates commercially pure titanium of JIS Class 1, CP2 indicates commercially pure titanium of JIS Class 2, and CP3 indicates commercially pure titanium of JIS Class 3. Underlined conditions in Table 2 indicate that the conditions are outside the scope of the present invention.

[0064]

[Table 2]

No.	Titanium substrate	Zinc salt		Calcium salt		HF content (mass%)	HNO ₃ content (mass%)	Temperature (°C)	Time (minutes)	Inert atmosphere annealing after cleaning step	Note
		Kind	Content (mass%)	Kind	Content (mass%)						
1	CP1	—	—	—	—	—	—	—	—	—	Comparative Example
2	CP1	—	—	—	—	2.0	4.5	40	1.0	—	Comparative Example
3	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
4	CP1	Zn(NO ₃) ₂	0.00092	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
5	CP1	ZnCl ₂	0.00096	Ca(NO ₃) ₂	0.00098	2.0	4.5	40	1.0	—	Present Invention Example
6	CP1	ZnCl ₂	0.00048	CaCl ₂	0.00072	2.0	4.5	40	1.0	—	Present Invention Example
7	CP1	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
8	CP1	ZnCl ₂	0.00096	CaCl ₂	<u>0.00036</u>	2.0	4.5	40	1.0	—	Comparative Example
9	CP1	ZnCl ₂	0.00129	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
10	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00163	2.0	4.5	40	1.0	—	Present Invention Example
11	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	1.0	4.0	40	1.0	—	Present Invention Example
12	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	6.0	10	40	1.0	—	Present Invention Example
13	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	<u>0.5</u>	<u>3.0</u>	40	1.0	—	Comparative Example
14	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	<u>8.0</u>	<u>12</u>	40	1.0	—	Comparative Example
15	CP1	ZnCO ₃	0.00104	CaCO ₃	0.00120	1.0	4.0	40	1.0	—	Present Invention Example
16	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	60	1.0	—	Present Invention Example
17	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	<u>30</u>	1.0	—	Comparative Example
18	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	<u>0.5</u>	—	Comparative Example
19	CP1	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	Ar, 500°C, 1.0 h	Present Invention Example
20	CP2	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
21	CP3	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
22	Ti-1Cu	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
23	Ti-3Al-2.5V	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
24	Ti-5Al-1Fe	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
25	Ti-0.05Pd	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
26	Ti-0.15Pd	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
27	Ti-15V-3Al-3Cr-3Sn	ZnCl ₂	0.00096	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Present Invention Example
28	CP2	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
29	CP3	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
30	Ti-1Cu	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
31	Ti-3Al-2.5V	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
32	Ti-5Al-1Fe	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
33	Ti-0.05Pd	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
34	Ti-0.15Pd	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example
35	Ti-15V-3Al-3Cr-3Sn	ZnCl ₂	<u>0.00024</u>	CaCl ₂	0.00108	2.0	4.5	40	1.0	—	Comparative Example

[0065]

Surface composition qualitative analysis, quantitative analysis, and depth-direction analysis were carried out by XPS on the surfaces of the samples that had been washed with water, and then washed with ultrasonic waves for 60 seconds by immersing the samples in acetone. Analysis conditions by XPS were as described below.

Apparatus: VersaProbe III manufactured by ULVAC-PHI, Inc.

X-ray source: mono-AlK α (hv: 1486.6 eV)

Beam diameter: 200 $\mu\text{m}\Phi$ ($\approx$ analysis region)

Detection depth: 2 to 8 nm

Sputtering conditions: Ar⁺, sputtering rate 2.0 nm/min. (SiO₂ conversion value)

The SiO₂ conversion value is the sputtering rate obtained under the same measurement conditions using a SiO₂ film the thickness of which has been measured in advance using an ellipsometer.

[0066]

(Color unevenness)

In order to evaluate color unevenness on the surface of a titanium material, L^{*}, a^{*}, and b^{*} were measured in accordance with JIS Z 8730: 2009 at a total of 10 points (5 points on each of the front and rear surfaces: 1 point at the sample central part and 4 points at the sample corner portions) on a 200 mmL $\times$ 300 mmw $\times$ 0.3 mmt sample after a water washing treatment, and color differences ΔE^*_{ab} between the measurement points were used as evaluation criteria. The color difference was obtained using the luminosity L^{*} and the chromaticities a^{*} and b^{*} at each measurement point obtained in accordance with JIS Z 8730:2009 from differences ΔL^* , Δa^* , and Δb^* , thereof between the measurement points in accordance with

$$\text{color difference } \Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}.$$

The color differences were measured with a light source C using a color difference meter CR-200b manufactured by Konica Minolta Japan Inc. Specifically, samples where the maximum value of the color differences ΔE^*_{ab} between the measurement points was 5 or less were determined to have favorable evaluation results (OK), and samples where the maximum value of the color differences ΔE^*_{ab} was more than 5 were determined to have poor evaluation results (NG).

[0067]

(Weather resistance)

A 50 mmL × 25 mmw × 0.3 mmt piece was cut out from the water-washed sample, and a discoloration acceleration test was carried out thereon. In the discoloration acceleration test, the sample was immersed in a sulfuric acid aqueous solution having a pH of 3 at 80°C for 4 days. $L^*a^*b^*$ of the surface of the titanium material before and after the discoloration acceleration test was measured to obtain color differences ΔE^*_{ab} before and after the discoloration acceleration test. The color differences were measured and calculated in the same manner as described above. The color differences were measured on the front and rear surfaces at 1 point in the central part and 4 points in the corner portions of the sample, and the color difference ΔE^*_{ab} obtained on average from a total of 10 points was used for the evaluation of weather resistance.

Since the threshold value of the color difference ΔE^*_{ab} at which discoloration is visually recognized is 8.0, in a case where the color difference ΔE^*_{ab} before and after the discoloration acceleration test was less than 8.0, the weather resistance was determined as favorable (OK), and, in a case where the color difference ΔE^*_{ab} before and after the discoloration acceleration test was 8.0 or more, the weather resistance was

determined as poor (NG).

[0068]

(Whiteness)

Furthermore, for the water-washed samples, L^* , a^* , and b^* were measured in accordance with JIS Z 8730:2009, and the whiteness was evaluated by comparing L^* , a^* , and b^* with L^* before the cleaning step. Regarding the measurement positions of the whiteness, the whiteness was measured on the front and rear surfaces at 1 point in the central part and 4 points in the corner portions of the sample in the same manner as described above, and L^* obtained on average from a total of 10 points was used for the evaluation of whiteness.

Since L^* (whiteness) of the sample before the cleaning step was about 65, whiteness that was different enough to be clearly recognized visually by comparing the sample before the cleaning step was used as an evaluation criterion. Specifically, samples having L^* of 70 or more were determined to have favorable evaluation results (OK), and samples having L^* of less than 70 were determined to have poor evaluation results (NG). The results are shown in Table 3. “-” in Table 3 indicates that the value was the detection limit or less. In addition, underlined conditions in the items of the XPS analysis and the surface oxide film in Table 3 indicate that the conditions are outside the scope of the present invention, and underlined numerical values in the items of the weather resistance, the color unevenness, and the whiteness in the same table indicate that the evaluation results were NG.

[0069]

[Table 3]

No.	XPS analysis		Surface oxide film			Weather resistance		Color unevenness		Whiteness		Note
	Zn content (atom%)	Ca content (atom%)	C content (atom%)	F content (atom%)	Thickness (nm)	Color difference ΔE^*ab	Evaluation result	Color difference ΔE^*ab	Evaluation result	L*	Evaluation result	
1	≒	≒	<u>22.8</u>	<u>8.1</u>	9	<u>20.0</u>	NG	0	OK	<u>65</u>	NG	Comparative Example
2	≒	<u>0.3</u>	3.1	3.0	10	<u>15.3</u>	NG	1.2	OK	74	OK	Comparative Example
3	0.3	0.7	3.1	5.0	11	6.8	OK	1.5	OK	74	OK	Present Invention Example
4	0.3	0.8	3.2	4.8	10	7.0	OK	1.3	OK	75	OK	Present Invention Example
5	0.3	0.7	3.1	4.9	9	7.1	OK	1.1	OK	77	OK	Present Invention Example
6	0.2	0.8	2.5	4.9	11	7.0	OK	0.9	OK	74	OK	Present Invention Example
7	≒	0.7	3.1	4.8	10	<u>14.0</u>	NG	1.1	OK	75	OK	Comparative Example
8	0.3	<u>0.1</u>	2.8	4.5	9	<u>15.0</u>	NG	1.2	OK	76	OK	Comparative Example
9	1.0	0.8	3.1	4.7	21	6.5	OK	<u>7.6</u>	NG	<u>62</u>	NG	Present Invention Example
10	0.4	1.5	3.0	4.9	22	5.7	OK	<u>9.8</u>	NG	<u>61</u>	NG	Present Invention Example
11	0.3	0.8	2.1	5.0	10	7.5	OK	0.8	OK	73	OK	Present Invention Example
12	0.4	0.8	3.3	5.0	9	7.8	OK	1.8	OK	75	OK	Present Invention Example
13	0.1	<u>0.4</u>	5.5	1.0	10	<u>18.0</u>	NG	1.2	OK	<u>68</u>	NG	Comparative Example
14	0.5	1.0	0.5	<u>23.4</u>	9	<u>25.4</u>	NG	1.5	OK	73	OK	Comparative Example
15	0.9	1.3	15.6	4.5	10	7.9	OK	1.4	OK	<u>65</u>	NG	Present Invention Example
16	0.4	0.8	3.2	5.0	11	7.3	OK	1.0	OK	75	OK	Present Invention Example
17	0.3	0.9	<u>23.4</u>	<u>7.5</u>	15	<u>21.3</u>	NG	<u>15.1</u>	NG	<u>54</u>	NG	Comparative Example
18	0.2	0.5	<u>24.3</u>	<u>8.2</u>	16	<u>19.8</u>	NG	<u>18.0</u>	NG	<u>55</u>	NG	Comparative Example
19	0.3	0.7	1.5	2.5	12	4.1	OK	0.7	OK	74	OK	Present Invention Example
20	0.4	0.6	2.0	5.0	10	6.5	OK	1.1	OK	74	OK	Present Invention Example
21	0.5	0.5	3.5	4.8	11	7.1	OK	1.5	OK	74	OK	Present Invention Example
22	0.6	0.8	5.0	3.0	10	6.5	OK	1.4	OK	75	OK	Present Invention Example
23	0.5	0.7	6.0	4.0	10	7.1	OK	1.2	OK	76	OK	Present Invention Example
24	0.6	0.7	3.0	4.5	11	7.5	OK	1.3	OK	74	OK	Present Invention Example
25	0.3	0.8	4.0	3.0	10	4.2	OK	1.6	OK	73	OK	Present Invention Example
26	0.4	0.5	4.5	3.0	10	3.0	OK	1.8	OK	75	OK	Present Invention Example
27	0.3	0.5	4.2	3.1	9	5.5	OK	1.4	OK	72	OK	Present Invention Example
28	≒	0.8	2.5	4.8	10	<u>15.1</u>	NG	0.8	OK	76	OK	Comparative Example
29	≒	0.5	3.5	4.9	10	<u>16.0</u>	NG	0.9	OK	75	OK	Comparative Example
30	≒	0.8	5.4	3.5	10	<u>15.5</u>	NG	1.1	OK	73	OK	Comparative Example
31	≒	0.7	7.0	4.1	10	<u>17.4</u>	NG	1.3	OK	75	OK	Comparative Example
32	≒	0.8	5.0	3.5	11	<u>18.0</u>	NG	1.2	OK	74	OK	Comparative Example
33	≒	1.0	4.0	4.5	10	<u>14.0</u>	NG	1.5	OK	76	OK	Comparative Example
34	≒	0.9	4.0	3.2	10	<u>13.8</u>	NG	1.4	OK	75	OK	Comparative Example
35	≒	0.8	5.6	4.8	9	<u>16.7</u>	NG	1.6	OK	72	OK	Comparative Example

[0070]

As shown in Tables 2 and 3, when the chemical composition of the surface of the titanium material analyzed by XPS was Zn: 0.1 atom% or more and Ca: 0.5 atom% or more, and the composition of the surface oxide film was C: 20.0 atom% or less and F: 5.0 atom% or less, the titanium materials were favorable in terms of weather resistance. Furthermore, the samples where the thickness of the surface oxide film was 5 to 20 nm were also favorable in terms of evaluation results of the color unevenness and the whiteness L^* .

[0071]

Hitherto, the preferable embodiment of the present invention has been described in detail, but the present invention is not limited to such examples. It is evident that a person skilled in the art of the present invention is able to conceive a variety of modification examples or correction examples within the scope of the technical concept described in the claims, and it is needless to say that such examples are also understood to be in the technical scope of the present invention.

CLAIMS

What is claimed is:

1. A titanium material,
wherein, when a chemical composition of a surface is analyzed by X-ray photoelectron spectroscopy, the titanium material contains, as a composition of the surface;
Zn: 0.1 atom% or more, and
Ca: 0.5 atom% or more, and
the titanium material contains, as a composition of a surface oxide film;
C: 20.0 atom% or less, and
F: 5.0 atom% or less.
2. The titanium material according to claim 1,
wherein the surface oxide film has a thickness of 5 to 20 nm.
3. A method for manufacturing a titanium material, comprising:
a cleaning step of cleaning a titanium raw material,
wherein the cleaning step includes;
an immersion treatment of immersing the titanium raw material in an aqueous solution having a temperature of 40°C to 60°C for 1.0 minutes or longer,
where the aqueous solution contains,
a zinc salt: 0.00030 to 0.65000 mass% in terms of Zn,
a calcium salt: 0.00060 to 0.40000 mass% in terms of Ca,
HF: 1.0 to 6.0 mass%, and
HNO₃: 4.0 to 10.0 mass%, and
a water washing treatment of washing the titanium raw material lifted from the aqueous solution with water.

4. The method for manufacturing a titanium material according to claim 3, wherein the zinc salt is 0.00030 to 0.00100 mass% in terms of Zn, and the calcium salt is 0.00060 to 0.00108 mass% in terms of Ca.
5. The method for manufacturing a titanium material according to claim 3 or 4, wherein the zinc salt is ZnCl_2 .
6. The method for manufacturing a titanium material according to claim 3 or 4, wherein the calcium salt is CaCl_2 .
7. The method for manufacturing a titanium material according to claim 5, wherein the calcium salt is CaCl_2 .
8. The method for manufacturing a titanium material according to claim 3 or 4, further comprising:
 - a heating step of heating the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere.
9. The method for manufacturing a titanium material according to claim 5, further comprising:
 - a heating step of heating the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere.
10. The method for manufacturing a titanium material according to claim 6, further comprising:
 - a heating step of heating the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere.
11. The method for manufacturing a titanium material according to claim 7, further comprising:

a heating step of heating the titanium raw material after the cleaning step to 300°C to 900°C in an inert atmosphere.