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(54) **TITANIUM ALLOY PLATE AND EXHAUST SYSTEM COMPONENT FOR AUTOMOBILES**

(57) This titanium alloy sheet has a predetermined chemical composition, in which a microstructure consists of an  $\alpha$ -phase and second phases, the average crystal grain size of the  $\alpha$ -phase is 3.0 to 10.0  $\mu\text{m}$ , the number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  is 25% or higher in the  $\alpha$ -phase, the number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  is 45% or higher

in the  $\alpha$ -phase, and in a case where 100 of 10  $\mu\text{m} \times 10 \mu\text{m}$  regions obtained by dividing a 100  $\mu\text{m} \times 100 \mu\text{m}$  region into 100 equal parts in a cross section are set to measurement regions and the number density of the second phases is obtained for each measurement region, the number of measurement regions in which 5 to 15 second phases are observed within each measurement region is 80 or more.

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**Description**

[Technical Field]

5     **[0001]**   The present disclosure relates to a titanium alloy sheet and an exhaust system component for automobiles.

[Background Art]

10     **[0002]**   Exhaust systems of four-wheeled automobiles and two-wheeled automobiles (hereinafter referred to as automobiles and the like) are equipped with an exhaust manifold and an exhaust pipe. Exhaust gas discharged from an engine and collected by an exhaust manifold is discharged to outside from an exhaust port at the rear of a vehicle body through an exhaust pipe. A catalyst device or a muffler (silencer) is placed in the middle of the exhaust pipe to purify exhaust gas and muffle exhaust noise. In the present specification, the term "exhaust system" is used throughout from the exhaust manifold to the exhaust pipe and the exhaust port. In addition, the components, such as exhaust manifolds, 15 exhaust pipes, catalyst devices, and mufflers, which constitute an exhaust system are referred to as "exhaust system components".

20     **[0003]**   In the related art, stainless steel having excellent corrosion resistance, high strength, excellent workability, and the like has been used for constituent members of exhaust systems for automobiles and the like. However, in recent years, a titanium material which is lighter than stainless steel and has high strength and excellent corrosion resistance has been used. For example, JIS Class 2 industrial pure titanium material is used for exhaust systems for two-wheeled automobiles. Furthermore, recently, titanium alloys having higher heat resistance have been used instead of the JIS Class 2 industrial pure titanium material.

25     **[0004]**   In particular, recently, the exhaust gas temperature has tended to increase. For this reason, the exhaust gas temperature of an exhaust pipe sometimes reaches about 800°C, and it is required for sufficient high-temperature strength to be ensured also in this temperature range. In addition, it is also desirable to inhibit high-temperature oxidation of exhaust system components (to have excellent oxidation resistance at a high temperature).

30     **[0005]**   In addition, even if the oxidation resistance and high-temperature strength are excellent, low workability makes it difficult to perform processing into components. For this reason, in a case where a titanium sheet is used for exhaust system components, it is also required to have favorable workability during forming.

35     **[0006]**   Patent Document 1 describes a titanium alloy with excellent high-temperature oxidation resistance which contains 0.15 to 2 mass% of Si with Al being limited to less than 0.30 mass% with the balance being titanium and unavoidable impurities.

40     **[0007]**   In addition, Patent Document 2 describes a titanium alloy with excellent corrosion resistance and high-temperature oxidation resistance, which contains Al: 0.30% to 1.50% and Si: 0.10% to 1.0% on a mass basis.

45     **[0008]**   In addition, Patent Document 3 describes a heat-resistant titanium alloy for exhaust system members with excellent cold workability which contains, by mass%, Cu: greater than 2.1% to 4.5%, oxygen: 0.04% or less, and Fe: 0.06% or less with the balance being Ti and unavoidable impurities.

50     **[0009]**   In addition, Patent Document 4 describes a titanium alloy material for exhaust system components with excellent oxidation resistance which contains, by mass%, Si: 0.1% to 0.6%, Fe: 0.04% to 0.2%, and O: 0.02% to 0.15% with the balance being Ti and unavoidable impurities, in which the total amount of Fe and O is 0.1% to 0.3% and the absolute amount of unavoidable impurities is less than 0.04%.

55     **[0010]**   However, the titanium alloys described in Patent Documents 1 to 4 are intended to ensure high-temperature strength by limiting the chemical components, and do not improve polishability.

60     **[0011]**   It is required for a titanium sheet for exhaust system components to have a glossy surface. In this case, the surface of the titanium sheet is polished to have a surface property that provides the required glossiness. As described in Patent Documents 1 to 4, techniques for improving high-temperature oxidation resistance, corrosion resistance, and cold workability while ensuring heat resistance are known. However, also improving polishability after product processing has not been examined.

[Citation List]

[Patent Document]

**[0012]**

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[Patent Document 1]

Japanese Unexamined Patent Application, First Publication No. 2007-270199

[Patent Document 2]

Japanese Unexamined Patent Application, First Publication No. 2005-290548  
 [Patent Document 3]  
 Japanese Unexamined Patent Application, First Publication No. 2009-030140  
 [Patent Document 4]  
 Japanese Unexamined Patent Application, First Publication No. 2013-142183

[Summary of the Invention]

[Problems to be Solved by the Invention]

**[0013]** The present disclosure has been made from the viewpoint of the above-described circumstances, and an object of the present disclosure is to provide a titanium alloy sheet and an exhaust system component for automobiles which have excellent workability, polishability, high-temperature oxidation resistance, and high-temperature strength.

[Means for Solving the Problem]

**[0014]**

[1] A titanium alloy sheet according to one aspect of the present disclosure has a chemical composition of, by mass%, Cu: 0.7% to 1.5%, Sn: 0.5% to 1.5%, Si: 0.10% to 0.60%, Nb: 0.1% to 1.0%, Zr: 0% to 1.0%, Cr: 0% to 0.5%, Mo: 0% to 0.5%, Al: 0% to 1.0%, Fe: limited to 0.08% or less, O: limited to 0.07% or less, and the balance of Ti and impurities, in which a microstructure consists of an  $\alpha$ -phase and second phases, the average crystal grain size of the  $\alpha$ -phase is 3.0 to 10.0  $\mu\text{m}$ , the number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  is 25% or higher in the  $\alpha$ -phase, the number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  is 45% or higher in the  $\alpha$ -phase, and in a case where 100 of 10  $\mu\text{m} \times 10 \mu\text{m}$  regions obtained by dividing a 100  $\mu\text{m} \times 100 \mu\text{m}$  region into 100 equal parts in a cross section are set to measurement regions and the number density of the second phases is obtained for each measurement region, the number of measurement regions in which 5 to 15 second phases are observed within each measurement region is 80 or more.

[2] In the titanium alloy sheet according to [1] above, the second phases may have an area proportion of 1.0% or higher.

[3] An exhaust system component for automobiles according to another aspect of the present disclosure includes the titanium alloy sheet according to [1] or [2] above.

[4] An exhaust system component for automobiles according to another aspect of the present disclosure is obtained by forming the titanium alloy sheet according to [1] or [2] above.

[Effects of the Invention]

**[0015]** According to the above-described aspects of the present disclosure, it is possible to provide a titanium alloy sheet and an exhaust system component for automobiles which have excellent workability, polishability, and high-temperature oxidation resistance.

[Embodiment for Implementing the Invention]

**[0016]** An exhaust system component for automobiles is obtained, for example, by press forming a titanium alloy sheet and is used in a high-temperature environment. In addition, it is required for a titanium alloy sheet for exhaust system components to have a glossy surface. Polishing the surface of a titanium alloy sheet may increase its glossiness, so the titanium alloy sheet is required to have good polishability.

**[0017]** In order to improve the polishability of a titanium alloy sheet, it is necessary to (1) have a flat surface before polishing and (2) reduce occurrence of tears originating from crystal grains during polishing.

**[0018]** Regarding (1) above, for example, if there are unevennesses or the like on the surface of the titanium alloy sheet caused by burning, the polishing time required to eliminate the unevennesses becomes long. That is, one method of improving the polishability is to make a sheet having a flat surface.

**[0019]** Regarding (2) above, one of the causes of impairing the appearance after polishing is that the hardness varies depending on the crystal orientation, resulting in different polished states for each crystal grain. Since it is not easy to control the crystal orientation to be significantly uniform, the crystal grains with different polished states are generally made inconspicuous through grain refining. However, sufficient polishability cannot be obtained unless the crystal grain size is not only made small but also made uniform. In addition, if the crystal grains are made too fine, the formability will deteriorate, so there is a limit to how fine the grains can be made.

**[0020]** In this manner, it is not easy to reduce the crystal grain size distribution while controlling the crystal grain size to be within the range in which the minimum formability is ensured, considering the non-uniformity in actual manufacturing. Therefore, the present inventors have conducted studies to reduce the difference in the polished state of crystal grains due to the crystal orientation. As a result, it has been found that, by forming intermetallic compounds with a predetermined number density or more as second phases within grains and at grain boundaries, the intermetallic compounds restrain the crystal grains and suppress deformation during polishing, resulting in more uniform polishing.

**[0021]** In addition, since exhaust system components become hot when in use, it is necessary to add alloying elements so as to ensure the high-temperature strength necessary for the exhaust system components. The present inventors have studied the chemical composition for ensuring high-temperature strength at 800°C.

**[0022]** As a result of intensive studies from the above viewpoints, the present inventors have completed the titanium alloy sheet of the present embodiment.

**[0023]** Hereinafter, a titanium alloy sheet according to one embodiment of the present disclosure (titanium alloy sheet of the present embodiment) and an exhaust system component for automobiles according to one embodiment of the present disclosure (exhaust system component for automobiles of the present embodiment) will be described.

**[0024]** The titanium alloy sheet of the present embodiment has a chemical composition of, by mass%, Cu: 0.7% to 1.5%, Sn: 0.5% to 1.5%, Si: 0.10% to 0.60%, Nb: 0.1% to 1.0%, Zr: 0% to 1.0%, Cr: 0% to 0.5%, Mo: 0% to 0.5%, Al: 0% to 1.0%, Fe: limited to 0.08% or less, O: limited to 0.07% or less, and the balance of Ti and impurities. In addition, in the titanium alloy sheet of the present embodiment, a microstructure consists of an  $\alpha$ -phase and second phases, the average crystal grain size of the  $\alpha$ -phase is 3.0 to 10.0  $\mu\text{m}$ , the number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  is 25% or higher in the  $\alpha$ -phase, the number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  is 45% or higher in the  $\alpha$ -phase. In addition, in the titanium alloy sheet of the present embodiment, in a case where 100 of 10  $\mu\text{m} \times 10 \mu\text{m}$  regions (sites) obtained by dividing a 100  $\mu\text{m} \times 100 \mu\text{m}$  region into 100 equal parts in a cross section are set to measurement regions and the number density of the second phases is obtained for each measurement region, the number of measurement regions in which 5 to 15 second phases are observed within each measurement region is 80 or more.

**[0025]** In addition, in the titanium alloy sheet of the present embodiment, it is preferable that an area proportion of the second phases is 1.0% or higher.

**[0026]** Further, the exhaust system component for automobiles of the present embodiment includes the above-described titanium alloy sheet.

**[0027]** First, the chemical composition of the titanium alloy sheet of the present embodiment will be described. "%" which is a unit of the amount of each element constituting the chemical composition means "mass%". In addition, a range indicated by sandwiching "to" includes values at both ends as a lower limit and an upper limit.

Cu: 0.7% to 1.5%

**[0028]** In order to ensure sufficient high-temperature strength, it is necessary for the Cu content to be set to 0.7% or more. The Cu content is preferably 0.8% or higher.

**[0029]** On the other hand, if the Cu content is greater than 1.5%, the workability deteriorates. In addition, there is a high likelihood that Cu will be segregated during ingot production. For this reason, the Cu content is set to 1.5% or less. The Cu content is preferably 1.4% or less, more preferably 1.3% or less, and still more preferably 1.2% or less.

Sn: 0.5% to 1.5%

**[0030]** In order to ensure sufficient high-temperature strength, it is necessary for the Sn content to be set to 0.5% or more. The Sn content is preferably 0.6% or more, more preferably 0.8% or more, and still more preferably 0.9% or more.

**[0031]** On the other hand, Sn can be contained in a relatively large amount because it hardly forms intermetallic compounds. However, excessive Sn content reduces workability and the solid solution limit of Cu and Si in the  $\alpha$ -phase. For this reason, it is necessary for the Sn content to be set to 1.5% or less. In addition, Sn is an element with high specific gravity, and even when added in large amounts, its contribution to solid solution strengthening is small because its atomic number proportion does not become so high. This is also the reason for restricting the upper limit of the amount thereof. The Sn content is preferably 1.4% or less, more preferably 1.3% or less, and still more preferably 1.2% or less.

Si: 0.10% to 0.60%

**[0032]** In order to ensure oxidation resistance and high-temperature strength, it is necessary for the Si content to be set to 0.10% or more. The Si content is preferably 0.15% or more and more preferably 0.20% or more.

**[0033]** On the other hand, if the Si content is greater than 0.60%, silicides are formed, grain growth is significantly

inhibited, and the workability decreases. For this reason, the Si content is set to 0.60% or less. The Si content is preferably 0.50% or less, more preferably 0.40% or less, still more preferably 0.35% or less, and still more preferably 0.30% or less.

Nb: 0.1% to 1.0%

**[0034]** In order to ensure oxidation resistance, it is necessary for the Nb content to be set to 0.1% or more. The Nb content is preferably 0.2% or more and more preferably 0.3% or more.

**[0035]** On the other hand, the higher the Nb content, the more the oxidation resistance is improved, but in addition to increasing the cost of raw materials, the effect of improving oxidation resistance reaches a plateau. For this reason, the Nb content is set to 1.0% or less. The Nb content is preferably 0.7% or less, more preferably 0.5% or less, and still more preferably 0.4% or less.

Zr: 0% to 1.0%

**[0036]** Zr is an element that facilitates formation of an intermetallic compound of Si and Ti. Zr is also present in the intermetallic compound that is formed. By containing Zr, a pinning effect can be easily obtained and grain growth can be suppressed due to a solute drag effect. For this reason, Zr may be contained as necessary. The Zr content is preferably 0.1% or more to obtain the above-described effect.

**[0037]** On the other hand, the incorporation of Zr lowers the  $\beta$  transformation point and reduces the promotion of formation of intermetallic compounds and the solute drag effect relative to the Zr content. For this reason, when Zr is contained, the amount thereof is set to 1.0% or less. The Zr content is preferably 0.8% or less, more preferably 0.6% or less, still more preferably 0.5% or less, and still more preferably 0.4% or less.

**[0038]** Since Zr is an optional element, the lower limit is 0%.

Cr: 0% to 0.5%

Mo: 0% to 0.5%

**[0039]** Cr and Mo are optional elements, and the amount thereof may be 0%. However, by containing Cr or Mo, grain growth is suppressed by the solute drag effect and high-temperature strength is improved. For this reason, these may be contained as necessary. The each of Cr content and Mo content is preferably set to 0.05% or more to obtain the above-described effect. The each of Cr content and Mo content is more preferably 0.1%.

**[0040]** On the other hand, when the Cr content or Mo content increases, the amount of  $\beta$ -phase is too high at high temperatures, resulting in a decrease in oxidation resistance. In addition, when the Mo content becomes excessive, workability will decrease. For this reason, when Mo is contained, the each of Cr content and Mo content is set to 0.5% or less. The each of Cr content or Mo content is preferably 0.4% or less and more preferably 0.3% or less.

Al: 0% to 1.0%

**[0041]** Al is an optional element. It may be 0%, but may be contained to ensure high-temperature strength. The Al content is preferably set to 0.1% or more to obtain the above-described effect.

**[0042]** On the other hand, if the Al content increases, the  $\alpha$ -phase is stabilized, the formation of the  $\beta$ -phase is suppressed, and the high-temperature strength and the oxidation resistance are further improved. However, the workability decreases, which is not preferable. In addition, the cold-rolling properties are greatly reduced. For this reason, when Al is contained, the Al content is set to 1.0% or less. The Al content is preferably 0.8% or less, more preferably 0.6% or less, and still more preferably 0.5% or less.

Fe: 0.08% or less

**[0043]** If the Fe content is too high, the  $\beta$ -phase is likely to be generated in a low temperature range. For this reason, additive elements are concentrated in the  $\beta$ -phase, the amount of solid solution elements in the  $\alpha$ -phase is reduced, and the high-temperature strength is reduced due to the increase in the  $\beta$ -phase proportion. In addition, the oxidation resistance may deteriorate due to the increase in the  $\beta$ -phase proportion. In addition, in a case where Cr and Mo are contained, narrowing of the range of the appropriate amount of Cr and Mo makes it difficult to control the chemical components of Cr and Mo. For this reason, the Fe content is preferable as low as possible, and it is necessary for the Fe content to be limited to 0.08% or less. The Fe content is preferably 0.06% or less and more preferably 0.04% or less.

O: 0.07% or less

**[0044]** O is an element that increases room-temperature strength but hardly improves the high-temperature strength. That is, when the O content increases, the high-temperature strength does not improve and the amount of springback increases, resulting in a decrease in workability. For this reason, the O content is preferably as low as possible. However, it is difficult to industrially reduce the oxygen (O) content, and a significant reduction increases raw material costs. For this reason, the amount thereof is about 0.04%, and is about 0.07% in consideration of variations. For this reason, the O content is limited to 0.07% or less.

One or more of Ni, V, Mn, Co, Ta, W, C, and N in amount of 0% to 0.05% each and in total of 0.30% or less

**[0045]** Ni, V, Mn, Co, Ta, and W all have a considerable effect of stabilizing the  $\beta$ -phase. For this reason, as in the present embodiment, in the titanium alloy sheet in which the  $\alpha$ -phase and the  $\beta$ -phase are controlled by Nb, Cr, and Mo, the amount of these elements are preferably low. In addition, if N and C are excessively contained, the  $\alpha$ -phase is stabilized and the strength at room temperature is increased, resulting in deterioration in workability. For this reason, the N content and C content is also preferably low. Accordingly, regardless of whether these elements are intentionally contained or contained as impurities, it is preferable that the amount of each element be 0.05% or less and the total amount of these elements be 0.30% or less.

**[0046]** Since the amount of these elements is preferably as low as possible, the lower limit of each amount and the total amount is 0%.

**[0047]** The balance of the titanium alloy sheet of the present embodiment is Ti and impurities other than the above.

**[0048]** Examples of other impurities include H and B. H is an element that forms a hydride together with Ti, and the formation of a hydride may embrittle the titanium alloy sheet. For this reason, even in the case where those elements are contained as impurities, it is preferable that the H content be suppressed as much as possible. In the titanium alloy sheet of the present embodiment, the H content is preferably 0.013% or less. There is a concern that B may form a coarse precipitate in an ingot. For this reason, even in the case where those elements are contained as impurities, it is preferable that the B content be suppressed as much as possible. In the titanium alloy sheet of the present embodiment, the B content is preferably set to 0.01% or less.

**[0049]** Next, the structure of the titanium alloy sheet of the present embodiment will be described.

**[0050]** The titanium alloy sheet of the present embodiment contains second phases and an  $\alpha$ -phase having an average crystal grain size of 3.0  $\mu\text{m}$  to 10.0  $\mu\text{m}$  in the structure. The second phases are structures other than the  $\alpha$ -phase and are mainly intermetallic compounds. The intermetallic compound of the present embodiment mainly contains  $\text{Ti}_2\text{Cu}$  and a silicide. There is a possibility that the  $\beta$ -phase may be contained in a second phase. However, even if the  $\beta$ -phase is contained therein, it is in very small amounts (for example, 0.2% or less). Therefore, the second phase may be regarded as an intermetallic compound. The  $\alpha$ -phase is a structure that occupies most of the microstructure (for example, 95% or more), and the remainder of the microstructure is the second phases.

Average crystal grain size of  $\alpha$ -phase: 3.0 to 10.0  $\mu\text{m}$

**[0051]** In the titanium alloy sheet of the present embodiment, a small average crystal grain size of the  $\alpha$ -phase means that a non-recrystallized portion remains. For this reason, in a case where the average crystal grain size of the  $\alpha$ -phase is small, workability decreases. The non-recrystallized portion causes unevenness in polishing, resulting in deterioration in polishability. For this reason, the average crystal grain size of the  $\alpha$ -phase is set to 3.0  $\mu\text{m}$  or more to prevent the non-recrystallized portion from occurring.

**[0052]** On the other hand, if the average crystal grain size of the  $\alpha$ -phase is excessively large, the polishability deteriorates. For this reason, it is necessary for the average crystal grain size of the  $\alpha$ -phase to be set to 10.0  $\mu\text{m}$  or less.

**[0053]** The average crystal grain size of the  $\alpha$ -phase can be obtained by the following method using EBSD.

**[0054]** Crystal grains of the  $\alpha$ -phase are uniformly dispersed. Accordingly, it may be measured at any position in the width direction, but the measurement may be performed, for example, on only the  $\alpha$ -phase to be measured in the center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width direction at a 1/2 length of the sheet width (at a 1/2 position of the sheet width in the sheet width direction from end portions of the sheet width direction) at an accelerating voltage of 15 kV, a magnification of 500 times or more, and a measurement pitch of 0.2  $\mu\text{m}$ . The measurement visual field is set so that one visual field contains 300 or more crystal grains or a total of 400 or more crystal grains are contained in a plurality of visual fields. The measurement sample is adjusted so that the average CI value becomes 0.2 or more. OIM-analysis™ (version 7.3.1) is used for measurement analysis software to obtain the crystal grain size of each crystal grain by regarding a boundary with a crystal orientation difference of 15° or more as a grain boundary and approximating the circle-equivalent diameter from the area of the crystal grains divided by this boundary. When calculating the crystal grain size, crystal grains having a crystal grain size of 1.0  $\mu\text{m}$  or less and

crystal grains that are incompletely included in the visual field are excluded. A crystal grain whose grain boundary is divided by the boundary of the field of view for measurement is determined as a crystal grain that is incompletely included in the visual field.

**[0055]** In a case where the sheet width direction is unclear, it can be determined through measurement on the surface. Since the material has a split-TD type texture, (0001) is strongly oriented at an angle of 30° to 40° in the sheet width direction. Accordingly, the directional axis where the position at which (0001) is strongly oriented is present in the measurement from the surface becomes the sheet width direction.

Crystal grain size distribution of  $\alpha$ -phase: Number proportion of crystal grains of which crystal grain size is average crystal grain size  $\pm 2 \mu\text{m}$  is 25% or more, and number proportion of crystal grains of which crystal grain size is average crystal grain size  $\pm 4 \mu\text{m}$  is 45% or more

**[0056]** Even if the average crystal grain size is 10.0  $\mu\text{m}$  or less, there is a possibility that coarse crystal grains may be slightly included. If the crystal grain size varies, the polished states of crystal grains will vary. Therefore, if crystal grains with a large difference in crystal grain size are included, a sufficient appearance cannot be obtained after polishing. Therefore, it is preferable to control the grain size distribution of the  $\alpha$ -phase in addition to the average crystal grain size of the  $\alpha$ -phase.

**[0057]** In the titanium alloy sheet of the present embodiment, in the  $\alpha$ -phase (among crystal grains constituting the  $\alpha$ -phase), the number proportion of the crystal grains of the  $\alpha$ -phase of which the crystal grain size is within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  (within a range of the average crystal grain size - 2  $\mu\text{m}$  to the average crystal grain size + 2  $\mu\text{m}$ ) is 25% or more to total, and the number proportion of the crystal grains of which the crystal grain size is within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  (within a range of the average crystal grain size - 4  $\mu\text{m}$  to the average crystal grain size + 4  $\mu\text{m}$ ) is 45% or more to total. Such a titanium alloy sheet is less likely to contain coarse crystal grains, thereby having improved polishability.

**[0058]** The upper limits of the number proportion of the crystal grains of the  $\alpha$ -phase of which the crystal grain size is within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  and the number proportion of the crystal grains of which the crystal grain size is within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  are not particularly limited, and may be 100% or lower than 100%.

**[0059]** The grain size distribution of the  $\alpha$ -phase is obtained through the following method.

**[0060]** Crystal grains of the  $\alpha$ -phase are uniformly dispersed. Accordingly, it may be measured at any position in the width direction. However, for example, a measurement region of the grain size distribution which is a rectangular region with one side length of 100  $\mu\text{m}$  or longer is set in the center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width direction at a 1/2 length of the sheet width such that 100 or more crystal grains are present in the region. The crystal orientation of the  $\alpha$ -phase for the measurement region is analyzed through the electron backscatter diffraction (EBSD). OIM-analysis™ (version 7.3.1) is used for analysis software to obtain the crystal grain size of each crystal grain by regarding a boundary with a crystal orientation difference of 15° or more as a grain boundary and approximating the circle-equivalent diameter from the area of the divided crystal grains.

**[0061]** Subsequently, the number proportion of the crystal grains of which the crystal grain size is within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  and the number proportion of the crystal grains of the  $\alpha$ -phase of which the crystal grain size is within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  are obtained from the crystal grain size of each of the obtained crystal grains and the average crystal grain size obtained through the method.

**[0062]** Accordingly, the grain size distribution of the crystal grains in the measurement region is obtained.

**[0063]** In a case where the sheet width direction is unclear, it can be determined through measurement on the surface. Since the material has a split-TD type texture, (0001) is strongly oriented at an angle of 30° to 40° in the sheet width direction. Accordingly, the directional axis where the position at which (0001) is strongly oriented is present in the measurement from the surface becomes the sheet width direction.

**[0064]** Distribution of number density of second phases: Among 100 measurement regions, number of measurement regions where 5 to 15 second phases are observed within each measurement region is 80 or more

**[0065]** Next, the distribution state of the second phases will be described.

**[0066]** In the titanium alloy sheet of the present embodiment, most of the microstructure consists of the  $\alpha$ -phase with the balance being the second phases. The second phases are mainly various intermetallic compounds. In a case of using a pinning effect or a solute drag effect to suppress grain growth of the  $\alpha$ -phase, it is necessary for the second phases or alloying elements to be uniformly present. By uniformly incorporating second phases, the grain growth of the  $\alpha$ -phase in a high-temperature environment when in use is prevented from being non-uniform, and the high-temperature strength is improved. However, if the second phases are non-uniformly distributed in the microstructure, the degree of grain growth of the  $\alpha$ -phase varies locally in the high-temperature region, and the high-temperature strength decreases. In addition, the non-uniform distribution of the second phases causes formation of a mixed grain structure even during annealing, and the formation of the mixed grain structure deteriorates the polishability and fatigue properties. Even if

the mixed grain structure is not formed, the non-uniform distribution of the second phases deteriorates the polishability. For this reason, it is necessary for the second phases to be uniformly distributed in the microstructure.

**[0067]** In the titanium alloy sheet of the present embodiment, the proportion of regions including a predetermined number of second phases which is obtained by measuring the number of the second phases in the plurality of measurement regions in the cross section of the titanium alloy sheet is used as an index of the uniformity of the distribution of the second phases.

**[0068]** Specifically, in a cross section perpendicular to the sheet width direction of a titanium alloy sheet at a 1/2 length of the sheet width, each region (100 regions each having one side of 10  $\mu\text{m}$ ) obtained by dividing the length of each side of a 100  $\mu\text{m}$  (100  $\mu\text{m} \times 100 \mu\text{m}$ ) region into 10 equal parts is regarded as a measurement region for the number density, and the number of second phases is obtained for each measurement region. Then, the number of measurement regions in which 5 to 15 second phases are observed (present) in each measurement region (10  $\mu\text{m} \times 10 \mu\text{m}$ ) among the 100 regions is obtained. If the number of measurement regions in which 5 to 15 second phases are observed within each measurement region is 80 or more, the second phases are considered to be uniformly distributed. Every measurement region may have 5 to 15 second phases. That is, the upper limit of the number of measurement regions in which 5 to 15 second phases are observed within each measurement region is 100. When calculating the number density of the second phases, in a case where there are second phases at boundaries of the divided regions, each second phase is divided by the number of adjacent regions. For example, in a case where a second phase is present across two regions, 0.5 is added for each of the two regions.

**[0069]** In a case where the distribution state of the second phases satisfies such a condition, the polishability is improved and a mixed grain structure of the  $\alpha$ -phase is less likely to be generated during high-temperature heating, thereby improving fatigue strength.

**[0070]** The number of regions in which 5 to 15 second phases are observed is obtained through the following method.

**[0071]** Since the  $\alpha$ -phase and the second phases are uniformly dispersed, the measurement position may be any position in the width direction. For example, the position of the region with one side of 100  $\mu\text{m}$  is set to match a center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width direction at a 1/2 length of the sheet width of a titanium alloy. 100 measurement regions are determined by dividing the length of each side of such a region into 10 equal parts. Each measurement region is observed with a scanning electron microscope (SEM), and the  $\alpha$ -phase is distinguished from the second phases using a reflection electron image. Since the second phases which are intermetallic compounds are fine precipitates which are whiter or blacker than the  $\alpha$ -phase which is a parent phase, these can be identified as second phases by this feature. The number of second phases within each measurement region is counted and obtained. This is carried out for 100 measurement regions, and the number of measurement regions in which the number of second phases is 5 to 15 is counted.

**[0072]** In a case where the sheet width direction is unclear, it can be determined through measurement on the surface. Since the material has a split-TD type texture, (0001) is strongly oriented at an angle of 30° to 40° in the sheet width direction. Accordingly, the directional axis where the position at which (0001) is strongly oriented is present in the measurement from the surface becomes the sheet width direction.

#### Area proportion of second phases

**[0073]** The area proportion of the second phases in the microstructure is preferably 0.01% or higher, more preferably 0.05% or higher, still more preferably 0.1% or higher, and still more preferably 1.0% or higher. If the second phases are present in an area proportion of 0.1% or higher, the polishability can be improved. In particular, by setting the area proportion of the second phases to 1.0% or more, the polishability can be further improved. On the other hand, in order to obtain sufficient workability, the upper limit of the area proportion of the second phases is preferably set to 3.0% or less and more preferably set to 2.0% or less.

**[0074]** The area proportion of the second phases is measured in the same region as that for the measurement of the number density of the second phases. That is, the above-described region with one side of 100  $\mu\text{m}$  (for example, prepared from the center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width direction at a 1/2 length of the sheet width of a titanium alloy) is observed with a scanning electron microscope (SEM), and the  $\alpha$ -phase and the second phases are discriminated using a reflection electron image. Since the second phases which are intermetallic compounds are fine precipitates which are whiter or blacker than the  $\alpha$ -phase which is a parent phase, these can be identified as second phases by this feature. Then, the area of the second phases within the region is measured to obtain the area proportion (%) of the second phases.

**[0075]** In addition, the microstructure of the titanium alloy sheet of the present embodiment is preferably an equiaxed structure. In a needle-like structure, regions with the same crystal orientation are macroscopically densely packed, so the polishability deteriorates. Specifically, the average aspect ratio (major axis length/minor axis length) of the  $\alpha$ -phase occupying most of the structure is preferably 3.0 or lower. As will be described below, needle-like crystal grains are once formed through heating above 830°C and at a  $\beta$  transformation point or higher in hot-rolled sheet annealing or intermediate

annealing. However, recrystallization occurs due to subsequent cold rolling and final annealing, whereby an equiaxed  $\alpha$ -phase is formed. The aspect ratio which is a (major axis length-to-minor axis length) ratio of  $\alpha$  crystal grains on an L-cross section of a titanium alloy sheet is obtained and is used as the average value of aspect ratios of 10 crystal grains.

**[0076]** The titanium alloy sheet of the present embodiment preferably has the following features.

Total elongation: 25.0% or more

**[0077]** Although it depends on the shape of parts after forming processing, it is necessary for at least the titanium alloy sheet to be able to be formed and welded into a tubular shape. After that, bending of the tube is required. Accordingly, the titanium alloy sheet of the present embodiment preferably has a total elongation of 25.0% or more to ensure sufficient workability during forming of parts. Although it is unnecessary for the upper limit of the total elongation to be limited, about 50.0% is industrially a substantial upper limit.

**[0078]** The total elongation is measured by performing a room-temperature tensile test. The tensile test at room temperature is performed by collecting an ASTM subsize tensile test piece (parallel portion width: 6.25 mm, parallel part length: 32 mm, and gauge length: 25 mm) of which the longitudinal direction is parallel to the rolling direction from the above-described titanium alloy sheet and setting the strain rate to 30 %/min. The test temperature is set to be within a range of 10°C to 35°C.

Erichsen value: 9.5 mm or more

**[0079]** The Erichsen test is a test that evaluates elements of deep drawing and bulging which are important in forming other than forming into shapes of the tubular shape. The titanium alloy sheet of the present embodiment preferably has an Erichsen value of 9.5 mm or more in consideration of the balance with the improvement in polishability.

**[0080]** The Erichsen value is measured according to an Erichsen test method specified in JIS Z 2247 (2006). The sheet thickness of the measurement sample is set to be within a range of 0.1 to 2.0 mm, and the width thereof is set to 90 mm or more. A tester is as described in JIS B 7729 (2005). As jig dimensions, dimensions for testing with standard specimens are used. However, a Teflon (registered trademark) sheet with a thickness of 50  $\mu\text{m}$  is used as a lubricant.

Oxidation resistance: oxidation mass gain of 5.0 mg/cm<sup>2</sup> or less after being held at 800°C for 100 hours in atmospheric air

**[0081]** Most commonly used exhaust system parts have an oxidation mass gain of 5.0 mg/cm<sup>2</sup> or less. Therefore, it is desirably to achieve the above oxidation mass gain even in a case where it is intended to be used at 800°C in the titanium alloy sheet of the present embodiment. For this reason, as an index of oxidation resistance, it is preferable that the oxidation mass gain after holding at 800°C for 100 hours in atmospheric air satisfy 5.0 mg/cm<sup>2</sup> or less.

**[0082]** A value obtained by collecting a 20 mm  $\times$  20 mm test piece from the above-described titanium alloy sheet, wet-polishing the surface thereof with emery paper #400, exposing it to static air at 800°C for 100 hours, measuring the mass gain after exposure, and dividing the mass gain by the surface area of the tensile test piece (mass gain (mg)/surface area of test piece (cm<sup>2</sup>)) is used as the oxidation mass gain. In a case where the oxidation test causes peeling-off of scales, it is necessary for the peeled-off scales to be included in the mass after exposure.

High-temperature strength (tensile strength): 26 MPa or more at 800°C

**[0083]** A material having an ensured high-temperature strength is required. In the present embodiment, the high-temperature strength in a temperature range in which use is assumed is thought to be important, and assuming application to exhaust system components that can handle higher exhaust gas temperatures, the titanium alloy sheet of the present embodiment preferably has a tensile strength of 26 MPa or more at 800°C.

**[0084]** The high-temperature strength (tensile strength) at 800°C is measured by performing a high-temperature tensile test. The high-temperature tensile test is performed by collecting a tensile test piece (parallel portion width: 10 mm, parallel part length and gauge length: 35 mm) of which the longitudinal direction is parallel to the rolling direction from the above-described titanium alloy sheet and setting the strain rate to 7.5 %/min. The test atmosphere is air at 800°C, and the test is performed after the test piece is held in the test atmosphere for 10 minutes so that the test piece sufficiently reaches a test temperature.

Polishability

**[0085]** The polishability is evaluated from glossiness after wet-polishing with emery paper #1500 and polishing with alumina buff for 60 minutes.

**[0086]** A polishing liquid used for alumina buff polishing is a solution obtained by adding 250 g of alumina powder with

an average particle size of 3  $\mu\text{m}$  in 1 liter of water. In the polishing test, samples are embedded in an epoxy resin with a diameter of 28 mm, and 6 samples are set in a holder of an automatic polishing device and polished with a pressing force of 60 N. The glossiness is measured according to a specular glossiness measurement method of JIS Z 8741 (1997).

[0087] The glossiness is measured with an incidence angle and an acceptance angle of 20°. From the viewpoint of polishability, the glossiness (Gs20) is preferably 920 or more.

[0088] The titanium alloy sheet of the present embodiment can be used as a material for an exhaust system component for automobiles. That is, the titanium alloy sheet of the present embodiment can be formed into a predetermined shape and welded to produce various exhaust system components for automobiles. Examples of the exhaust system component for automobiles of the present embodiment include components such as exhaust manifolds, exhaust pipes, catalyst devices, and mufflers, and the titanium alloy sheet of the present embodiment can be used as a material for these components. These exhaust system components can be used not only for four-wheeled automobiles but also for two-wheeled automobiles.

[0089] The sheet thickness of the titanium alloy sheet of the present embodiment is not limited, but is preferably 0.5 to 2.0 mm when used as a material for exhaust system components for automobiles. The sheet thickness thereof is preferably 0.6 to 1.5 mm.

[0090] Next, a method for manufacturing the titanium alloy sheet of the present embodiment will be described.

[0091] In the conventional process of manufacturing a titanium alloy sheet, a coil is manufactured through hot rolling after an ingot which has a predetermined chemical composition and is manufactured through electron beam melting, vacuum arc melting, or the like is subjected to a blooming process (forging or rolling) for the purpose of destroying a solidified structure at a temperature in a  $\beta$  single-phase range. This coil is annealed as necessary, and cold rolling and annealing are repeated as necessary after descaling.

[0092] In general, a microstructure composed of equiaxed grains has an excellent balance between strength and workability. In order to obtain a microstructure composed of equiaxed grains and to achieve excellent cold-rolling properties, annealing is generally performed below the  $\beta$  transformation point after hot rolling. However, there are an  $\alpha$ -phase and second phases below the  $\beta$  transformation point, and element distribution occurs between the  $\alpha$ -phase and the second phases. In particular, the higher the temperature, the faster the element distribution occurs. If the element distribution occurs, distribution of second phases becomes non-uniform.

[0093] The distribution of alloying elements in titanium alloys is homogenized to some extent during the blooming process from the distribution state occurring during solidification (ingot production). However, the temperature is sometimes below the  $\beta$  transformation point at the completion of the process although heating is performed in a  $\beta$  single-phase range during the blooming process. In addition, even if the temperature does not fall below the  $\beta$  transformation point, the cooling rate is very slow, and distribution occurs during cooling. Even if, for example, cooling is performed after bloom rolling to increase the cooling rate, there is a large difference in cooling rate between the inside and the surface layer portion, and the element distribution always occurs to some extent in the inside where the cooling rate is low.

[0094] In addition, even if a slab is heated at the  $\beta$  transformation point or higher before hot rolling to eliminate the element distribution, the temperature decreases during hot rolling and becomes below the  $\beta$  transformation point, and the element distribution proceeds during hot rolling. In addition, since it is necessary to maintain the temperature for a long period of time to raise the temperature to the  $\beta$  transformation point or higher to the inside of the slab, a surface-hardened layer is formed due to oxidation, resulting in a decrease in cold-rolling properties.

[0095] In the present embodiment, at least one of hot-rolled sheet annealing and intermediate annealing which has conventionally been performed below the  $\beta$  transformation point is performed at the  $\beta$  transformation point or higher, and cooling is performed so that the element distribution is reduced and the average cooling rate from an annealing temperature to 700°C is 5 °C/second or higher to obtain a titanium alloy sheet with reduced element distribution. Unlike the blooming process, it is possible to suppress the element distribution in both the surface and the inside by heating the hot-rolled sheet in which a thickness is made to thin at a  $\beta$  transformation point or higher after the hot-rolled sheet is made into one with reduced thickness. The alloying elements can be more uniformly distributed by performing both hot-rolled sheet annealing and intermediate annealing at a  $\beta$  transformation point or higher.

[0096] In most cases, the titanium alloy sheet of the present embodiment has a  $\beta$  transformation point of higher than 830°C.

[0097] That is, the titanium alloy sheet of the present embodiment can be manufactured through a manufacturing method including the following processes.

(I) Hot rolling process of hot rolling an ingot made of titanium alloy having above-described chemical components to obtain hot-rolled sheet

(II) Hot-rolled sheet annealing process of annealing (hot-rolled sheet annealing) hot-rolled sheet as necessary

(III) Cold rolling process of cold rolling hot-rolled sheet at rolling reduction of 60% or higher.

However, intermediate annealing may be performed as necessary before final reduction.

(IV) Final annealing process of performing final annealing on titanium alloy sheet after cold rolling process at soaking

temperature of 550°C or higher and lower than 670°C for 1 minute to 24 hours

**[0098]** However, at least one of hot-rolled sheet annealing and intermediate annealing in the cold rolling process is performed, and the annealing temperature is set to be higher than 830°C and a  $\beta$  transformation point or higher.

**[0099]** Hereinafter, each of the processes of the manufacturing conditions will be described.

<Hot rolling process>

**[0100]** In the hot rolling process, an ingot made of a titanium alloy having above-described chemical components is hot rolled to obtain hot-rolled sheet.

**[0101]** The hot rolling conditions are not particularly limited and may be well-known conditions.

**[0102]** Processes prior to the hot rolling process are not particularly limited. For example, a hot-rolled sheet may be manufactured through hot rolling after an ingot which has a predetermined chemical composition and is manufactured through electron beam melting, vacuum arc melting, or the like is subjected to a blooming process (forging or rolling) for the purpose of destroying a solidified structure in a  $\beta$  single-phase range.

<Hot-rolled sheet annealing process>

**[0103]** In a case where the hot-rolled sheet obtained through hot rolling is subjected to hot-rolled sheet annealing, it is preferable that the annealing temperature be higher than 830°C and a  $\beta$  transformation point or higher, the annealing time be 1 to 5 minutes, and the average cooling rate from an annealing temperature to 700°C be 5 °C/second or higher.

**[0104]** By setting the annealing temperature to be higher than 830°C and a  $\beta$  transformation point or higher and the annealing time to be 1 minute or longer, the element distribution can be suppressed, the alloying elements can be more uniformly distributed, and second phases can be uniformly distributed. On the other hand, if the annealing time is longer than 5 minutes, the yield is lowered due to oxidation and the productivity is lowered due to the longer period of time, which is not preferable. Although it is unnecessary for the upper limit of the annealing temperature to be limited, the annealing temperature is preferably 1000°C or lower from the viewpoint of the reduction in yield due to oxidation.

**[0105]** In addition, if the average cooling rate from an annealing temperature to 700°C is slow, element distribution may occur during cooling. For this reason, the average cooling rate from an annealing temperature to 700°C is set to 5 °C/second or higher. Since the degree of element distribution does not greatly affect distribution of second phases even if the average cooling rate is increased, the upper limit is not necessarily specified, but may be 300 °C/second or lower.

**[0106]** However, in a case where intermediate annealing to be described below is performed under the conditions of an annealing temperature of higher than 830°C and a  $\beta$  transformation point or higher, an annealing time of 1 to 5 minutes, and the average cooling rate from an annealing temperature to 700°C of 5 °C/second or higher, the hot-rolled sheet annealing process may not be performed or may be performed under conditions other than those described above.

<Cold rolling process>

**[0107]** In the cold rolling process, cold rolling is performed on the hot-rolled sheet after the hot rolling process or the hot-rolled sheet after the hot-rolled sheet annealing process. In a case of performing cold rolling on the hot-rolled sheet, since it is necessary to obtain fine equiaxed grains after final annealing, the rolling reduction in the cold rolling (cumulative rolling reduction in a case of a plurality of passes) is set to 60% or higher. The rolling reduction in the cold rolling may suffice to be 90% or lower to prevent cracks. In a case of performing intermediate annealing to be described below, the rolling reduction in the cold rolling before intermediate annealing is regarded as an intermediate cold rolling reduction ratio, the rolling reduction in the cold rolling after intermediate annealing is regarded as a final cold rolling reduction ratio, and the final cold rolling reduction ratio is set to 60% or higher.

**[0108]** In addition, in the hot-rolled sheet annealing, in a case where annealing is performed at a temperature higher than 830°C and at a  $\beta$  transformation point or higher, the microstructure becomes a needle-like structure and the cold-rolling properties are reduced. For this reason, in this case, as the conditions for the cold rolling, the rolling reduction from a first pass to a second pass is preferably set to 10% or lower and the rolling reduction thereafter is preferably set to 15% or less. By performing processing at a low rolling reduction up to the second pass, cold rolling can be stably performed without causing cracks. Thereafter, the temperature rises due to heat generated by the processing, cracks are less likely to occur even if the rolling reduction is increased.

**[0109]** In a case where hot-rolled sheet annealing is not performed, in the cold rolling process, cold rolling is interrupted before final reduction, and intermediate annealing is performed. In a case of performing intermediate annealing, it is preferable that the annealing temperature be higher than 830°C and a  $\beta$  transformation point or higher, the annealing time be 1 to 5 minutes, and the average cooling rate from an annealing temperature to 700°C be 5 °C/second or higher.

**[0110]** Reasons for these conditions are the same as the reasons described in the hot-rolled sheet annealing.

**[0111]** Even in a case of performing hot-rolled sheet annealing, the above-described intermediate annealing may be performed.

**[0112]** As described above, by setting either annealing temperature of hot-rolled sheet annealing or final intermediate annealing to a temperature higher than 830°C and higher than or equal to a  $\beta$  transformation point, the element distribution can be suppressed, the alloying elements can be more uniformly distributed, and second phases can be uniformly distributed. In particular, by setting the annealing temperature of at least the intermediate annealing to a temperature higher than or equal to a  $\beta$  transformation point, the heating is performed at a  $\beta$  transformation point or higher in a state where the sheet thickness is reduced, and the element distribution can be suppressed on the surface and the inside of the sheet. Furthermore, by performing both hot-rolled sheet annealing and intermediate annealing above 830°C and at a  $\beta$  transformation point or higher, the element distribution can be suppressed and the alloying elements can be more uniformly distributed.

<Final annealing process>

**[0113]** The titanium alloy sheet after the cold rolling process is subjected to final annealing in a temperature range of higher than or equal to 550°C and lower than 670°C for recrystallization. If the annealing temperature is lower than 550°C, a large amount of intermetallic compounds is produced, so that recrystallization does not proceed sufficiently, resulting in formation of non-recrystallized regions and reduction in polishability. In addition, if the annealing temperature is higher than or equal to 670°C, there is a concern that the  $\alpha$ -phase grains will grow to form coarse crystal grains. For this reason, the final annealing is performed at a temperature lower than 670°C.

**[0114]** The annealing time for the final annealing is 1 minute to 24 hours. By setting the annealing time to 1 minute or longer, recrystallization sufficiently proceeds. In addition, by setting the annealing time to 24 hours or shorter, the formation of coarse crystal grains is prevented. The cooling rate (cooling rate in the temperature range below 550°C) after the final annealing is not particularly limited.

**[0115]** Next, the exhaust system component for automobiles of the present embodiment will be described.

**[0116]** The exhaust system component for automobiles of the present embodiment includes (or in some cases, consists of) the above-described titanium alloy sheet. The exhaust system component for automobiles of the present embodiment is obtained by forming the titanium alloy sheet of the present embodiment, for example, by press forming. Since the chemical composition does not change due to forming, the chemical composition of the exhaust system component for automobiles is the same as that of the titanium alloy sheet of the present embodiment. In a case where a titanium alloy sheet is formed into an exhaust system component for automobiles, twinning deformation occurs due to the forming, so that the crystal grain size is fine in the portion that has been deformed by the forming. The twinning deformation can be identified through OIM analysis. However, when the workability increases, the crystal orientation difference between a parent phase and twinning deformation changes, which makes analysis difficult. For this reason, in order to identify the crystal grain size of the  $\alpha$ -phase, it is necessary to prepare a measurement sample from a portion of an exhaust system component for automobiles which has an appropriate working degree.

[Examples]

**[0117]** A titanium alloy having a chemical composition shown in Table 1 was made into an ingot through vacuum arc button melting. The produced ingot was hot rolled at 1000°C to obtain a hot-rolled sheet with a thickness of 10 mm. Thereafter, hot rolling was performed at 860°C to obtain a hot-rolled sheet with a thickness of 4.0 mm. In Table 1, description of the amount of each of Ni, V, Mn, Co, Ta, W, C, and N was omitted, and the total amount of these elements was described in the "others" column. In all cases, the amount of each of these elements was 0.05% or less. In addition, in all cases, the H content among the impurities was 0.013% or less.

**[0118]** Thereafter, a descaling process or a descaling process after performing hot-rolled sheet annealing as necessary at a temperature and a time described in Table 2 was carried out. Then, intermediate annealing was performed as necessary along with cold rolling, and final cold rolling was performed. Furthermore, final annealing was performed. In this manner, titanium alloy sheets No. 1 to No. 48 were manufactured.

**[0119]** Furthermore, polishing treatment was performed on the obtained titanium alloy sheets. As the polishing treatment, wet polishing was performed with emery paper #1500 and polishing with alumina buff was performed for 60 minutes. As a polishing liquid used for alumina buff polishing, a solution obtained by adding 250 g of alumina powder with an average particle size of 3  $\mu\text{m}$  in 1 liter of water was used. In the polishing treatment, samples were embedded in an epoxy resin with a diameter of 28 mm, and 6 samples were set in a holder of an automatic polishing device and polished with a pressing force of 60 N.

**[0120]** Various evaluations were performed on the titanium alloy sheets after polishing.

**[0121]** The average crystal grain size of an  $\alpha$ -phase was measured for the  $\alpha$ -phase only using EBSD as described above in the center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width

direction at a 1/2 length of the sheet width at an accelerating voltage of 15 kV, a magnification of 500 times, and a measurement pitch of 0.2  $\mu\text{m}$ . The measurement visual field was set so that one visual field contains 300 or more crystal grains or a total of 400 or more crystal grains were contained in a plurality of visual fields, and the measurement samples were adjusted so that the average CI value became 0.2 or more. OIM-analysis™ (version 7.3.1) was used for measurement analysis software to obtain the crystal grain size of each crystal grain by regarding a boundary with a crystal orientation difference of 15° or more as a grain boundary and approximating the circle-equivalent diameter from the area of the crystal grains divided by this boundary. When calculating the crystal grain size, crystal grains having a crystal grain size of 1.0  $\mu\text{m}$  or less and crystal grains that were incompletely included in the visual field were excluded.

**[0122]** For the grain size distribution of the  $\alpha$ -phase, as described above, the measurement region (a rectangular region with one side length of 100  $\mu\text{m}$  or longer: prepared from the center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width direction at a 1/2 length of the sheet width) set when measuring the average crystal grain size was used as a measurement region of the grain size distribution. The crystal orientation of the  $\alpha$ -phase for the measurement region was analyzed through the electron backscatter diffraction (EBSD). OIM-analysis™ (version 7.3.1) was used for analysis software to obtain the crystal grain size of each crystal grain by regarding a boundary with a crystal orientation difference of 15° or more as a grain boundary and approximating the circle-equivalent diameter from the area of the divided crystal grains. Subsequently, the number proportion of the crystal grains of the  $\alpha$ -phase of which the crystal grain size is within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  and the number proportion of the crystal grains of the  $\alpha$ -phase of which the crystal grain size is within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  are obtained from the crystal grain size of each of the obtained crystal grains and the average crystal grain size obtained through the method.

**[0123]** For the distribution state of the second phases, as described above, in the center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width direction at a 1/2 length of the sheet width, each region obtained by dividing a region with one side of 100  $\mu\text{m}$  into  $10 \times 10$  equal sections was used as a measurement region (100 regions each having one side of 10  $\mu\text{m}$  were used as measurement regions), the number of second phases per unit area was obtained for each measurement region, and the number of measurement regions in which 5 to 15 second phases were observed was obtained.

**[0124]** The measurement regions were observed with a scanning electron microscope (SEM), and the  $\alpha$ -phase was distinguished from the second phases using a reflection electron image. Since the second phases which were intermetallic compounds were fine precipitates which were whiter or blacker than the  $\alpha$ -phase which was a parent phase, these could be identified as second phases by this feature.

**[0125]** The area proportion of the second phases was measured in the same region as that for the number density of the second phases. The above-described region with one side of 100  $\mu\text{m}$  (in the center portion of the sheet thickness of a cross section (L-cross section) perpendicular to the sheet width direction at a 1/2 length of the sheet width) was observed with a scanning electron microscope (SEM), and the  $\alpha$ -phase and the second phases were discriminated using a reflection electron image. Then, the area of the second phases within the region was measured to obtain the area proportion (%) of the second phases.

**[0126]** The total elongation was measured by performing a room-temperature tensile test. The tensile test at room temperature was performed by collecting an ASTM subsize tensile test piece (parallel portion width: 6.25 mm, parallel part length: 32 mm, and gauge length: 25 mm) of which the longitudinal direction was parallel to the rolling direction from the above-described titanium alloy sheet and setting the strain rate to 30 %/min. The test temperature was set to be within a range of 10°C to 35°C.

**[0127]** The Erichsen value was measured according to an Erichsen test method specified in JIS Z 2247 (2006). The sheet width of each measurement sample was set to 90 mm or more. A tester was as described in JIS B 7729 (2005). A Teflon (registered trademark) sheet with a thickness of 50  $\mu\text{m}$  was used as a lubricant. As jig dimensions, dimensions for testing with standard specimens were used.

**[0128]** A total elongation of 25.0% or more and an Erichsen value of 9.5 mm or more were determined to be excellent in workability.

**[0129]** A value obtained by collecting a 20 mm  $\times$  20 mm test piece from the titanium alloy sheet, wet-polishing the surface thereof with emery paper #400, exposing it to static air at 800°C for 100 hours, measuring the mass gain after exposure, and dividing the mass gain by the surface area of the tensile test piece (mass gain (mg)/surface area of test piece ( $\text{cm}^2$ )) was used as the oxidation mass gain. In a case where the oxidation test caused peeling-off of scales, the peeled-off scales were included in the mass after exposure. An oxidation mass gain of 5.0 mg/ $\text{cm}^2$  or less was determined to be excellent in at high-temperature oxidation resistance.

**[0130]** The high-temperature strength (tensile strength) at 800°C was measured by performing a tensile test by collecting a tensile test piece (parallel portion width: 10 mm, parallel part length and gauge length: 35 mm) of which the longitudinal direction is parallel to the rolling direction from the above-described titanium alloy sheet and setting the strain rate to 7.5 %/min. The test atmosphere was air at 800°C, and the test was performed after the test piece was held in the test atmosphere for 10 minutes so that the test piece sufficiently reached a test temperature. A high-temperature

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strength (tensile strength) of 26 MPa or more at 800°C was determined to be excellent.

**[0131]** The glossiness (Gs20) was measured according to a specular glossiness measurement method of JIS Z 8741 (1997). The glossiness was measured with an incidence angle and an acceptance angle of 20°. A glossiness Gs20 of 920 or more was determined to be excellent in polishability.

5 **[0132]** The evaluation results are shown in Table 3.

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[Table 1]

| No. | Component No. | Chemical composition (mass%: balance being Ti and impurities) |     |      |     |     |     |     |     |      |      |        | β transformation point (°C) |
|-----|---------------|---------------------------------------------------------------|-----|------|-----|-----|-----|-----|-----|------|------|--------|-----------------------------|
|     |               | Cu                                                            | Sn  | Si   | Nb  | Zr  | Mo  | Cr  | A1  | Fe   | O    | Others |                             |
| 1   | A             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     |     |     |     | 0.03 | 0.07 | <0.10  | 890                         |
| 2   | B             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     |     |     |     | 0.08 | 0.07 | <0.10  | 890                         |
| 3   | C             | 0.7                                                           | 1.0 | 0.30 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 4   | D             | 1.5                                                           | 1.0 | 0.30 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 885                         |
| 5   | E             | 1.0                                                           | 0.5 | 0.30 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 6   | F             | 1.0                                                           | 1.5 | 0.30 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 7   | G             | 1.0                                                           | 1.0 | 0.10 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 8   | H             | 1.0                                                           | 1.0 | 0.60 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 9   | I             | 1.0                                                           | 1.0 | 0.05 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 10  | J             | 1.0                                                           | 1.0 | 0.65 | 0.4 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 11  | K             | 1.0                                                           | 1.0 | 0.30 | 0.1 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 12  | L             | 1.0                                                           | 1.0 | 0.30 | 1.0 |     |     |     |     | 0.03 | 0.05 | <0.10  | 890                         |
| 13  | M             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     |     |     | 1.0 | 0.03 | 0.05 | <0.10  | 910                         |
| 14  | N             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     |     |     | 1.5 | 0.03 | 0.05 | <0.10  | 915                         |
| 15  | O             | 1.0                                                           | 1.0 | 0.30 | 0.4 | 1.0 |     |     |     | 0.03 | 0.05 | <0.10  | 880                         |
| 16  | P             | 1.0                                                           | 1.0 | 0.30 | 0.4 | 1.5 |     |     |     | 0.03 | 0.05 | <0.10  | 875                         |
| 17  | Q             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     |     | 0.5 |     | 0.03 | 0.05 | <0.10  | 885                         |
| 18  | R             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     |     | 0.7 |     | 0.03 | 0.05 | <0.10  | 880                         |
| 19  | S             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     | 0.5 |     |     | 0.03 | 0.05 | <0.10  | 885                         |
| 20  | T             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     | 0.7 |     |     | 0.03 | 0.05 | <0.10  | 880                         |
| 21  | U             | 1.0                                                           | 1.0 | 0.30 | 0.4 | 0.5 | 0.3 | 0.3 |     | 0.03 | 0.05 | <0.10  | 875                         |
| 22  | V             | 1.0                                                           | 1.0 | 0.30 | 0.4 | 0.5 |     |     | 0.5 | 0.03 | 0.05 | <0.10  | 900                         |
| 23  | W             | 1.0                                                           | 1.0 | 0.30 | 0.4 |     | 0.3 |     | 1.0 | 0.03 | 0.05 | <0.10  | 905                         |
| 24  | X             | 1.0                                                           | 1.0 | 0.30 | 0.4 | 0.5 |     | 0.3 |     | 0.03 | 0.05 | <0.10  | 875                         |

(continued)

| No. | Component No. | Chemical composition (mass%: balance being Ti and impurities) |            |      |            |     |    |    |     |      |      | β transformation point (°C) |        |
|-----|---------------|---------------------------------------------------------------|------------|------|------------|-----|----|----|-----|------|------|-----------------------------|--------|
|     |               | Cu                                                            | Sn         | Si   | Nb         | Zr  | Mo | Cr | A1  | Fe   | O    |                             | Others |
| 25  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 26  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 27  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 28  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 29  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 30  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 31  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 32  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 33  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 34  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 35  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 36  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 37  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 38  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 39  | Y             | 1.0                                                           | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 40  | Z             | <u>0.5</u>                                                    | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 895    |
| 41  | AA            | <u>2.0</u>                                                    | 1.0        | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 885    |
| 42  | AB            | 1.0                                                           | <u>0.4</u> | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 43  | AC            | 1.0                                                           | <u>2.0</u> | 0.30 | 0.4        |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 44  | AD            | 1.0                                                           | 1.0        | 0.30 | <u>0.0</u> |     |    |    |     | 0.03 | 0.06 | <0.10                       | 890    |
| 45  | AE            | 1.0                                                           | 1.0        | 0.30 | 0.4        | 1.0 |    |    | 0.5 | 0.03 | 0.07 | <0.10                       | 890    |
| 46  | AF            | 1.0                                                           | 0.5        | 0.10 | 0.4        |     |    |    |     | 0.03 | 0.07 | <0.10                       | 880    |
| 47  | AG            | 1.2                                                           | 1.2        | 0.20 | 0.2        |     |    |    |     | 0.03 | 0.07 | <0.10                       | 890    |

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(continued)

| No. | Component No. | Chemical composition (mass%: balance being Ti and impurities) |     |      |     |    |    |    |    |      |      |        | $\beta$ transformation point (°C) |
|-----|---------------|---------------------------------------------------------------|-----|------|-----|----|----|----|----|------|------|--------|-----------------------------------|
|     |               | Cu                                                            | Sn  | Si   | Nb  | Zr | Mo | Cr | A1 | Fe   | O    | Others |                                   |
| 48  | AH            | 0.8                                                           | 0.8 | 0.40 | 0.2 |    |    |    |    | 0.03 | 0.07 | <0.10  | 890                               |

The underlines indicate that the results are out of the range of the present invention.

[Table 2]

| No. | Component No. | β transformation point (°C) | Hot-rolled sheet annealing |            |                        | Intermediate cold rolling reduction ratio (%) | Intermediate annealing |            |                        | Rolling reduction in cold rolling *2 (%) | Final annealing  |            |                 |
|-----|---------------|-----------------------------|----------------------------|------------|------------------------|-----------------------------------------------|------------------------|------------|------------------------|------------------------------------------|------------------|------------|-----------------|
|     |               |                             | Temperature (°C)           | Time (min) | Cooling rate *1 (°C/s) |                                               | Temperature (°C)       | Time (min) | Cooling rate *1 (°C/s) |                                          | Temperature (°C) | Time (min) | Cooling         |
| 1   | A             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 2   | B             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 3   | C             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 4   | D             | 885                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 5   | E             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 6   | F             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 7   | G             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 8   | H             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 9   | I             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 10  | J             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 11  | K             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 12  | L             | 890                         | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 13  | M             | 910                         | 920                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |

(continued)

| No. | Component No. | $\beta$ transformation point (°C) | Hot-rolled sheet annealing |            |                        | Intermediate cold rolling re-duction ratio (%) | Intermediate annealing |            |                        | Rolling re-duction in cold rolling *2 (%) | Final annealing  |            |                 |
|-----|---------------|-----------------------------------|----------------------------|------------|------------------------|------------------------------------------------|------------------------|------------|------------------------|-------------------------------------------|------------------|------------|-----------------|
|     |               |                                   | Temperature (°C)           | Time (min) | Cooling rate *1 (°C/s) |                                                | Temperature (°C)       | Time (min) | Cooling rate *1 (°C/s) |                                           | Temperature (°C) | Time (min) | Cooling         |
| 14  | N             | 915                               | 920                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 15  | O             | 880                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 16  | P             | 875                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 17  | Q             | 885                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 18  | R             | 880                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 19  | S             | 885                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 20  | T             | 880                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 21  | U             | 875                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 22  | V             | 900                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 23  | W             | 905                               | 910                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 24  | X             | 875                               | 900                        | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |
| 25  | Y             | 890                               | 900                        | 1          | 5                      | 50                                             | 900                    | 1          | 5                      | 60                                        | 660              | 480        | Furnace cooling |
| 26  | Y             | 890                               | <u>800</u>                 | 1          | 5                      | -                                              | -                      | -          | -                      | 60                                        | 660              | 480        | Furnace cooling |

(continued)

| No. | Component No. | $\beta$ transformation point (°C) | Hot-rolled sheet annealing |            |                        | Intermediate cold rolling reduction ratio (%) | Intermediate annealing |            |                        | Rolling reduction in cold rolling *2 (%) | Final annealing  |            |                 |
|-----|---------------|-----------------------------------|----------------------------|------------|------------------------|-----------------------------------------------|------------------------|------------|------------------------|------------------------------------------|------------------|------------|-----------------|
|     |               |                                   | Temperature (°C)           | Time (min) | Cooling rate *1 (°C/s) |                                               | Temperature (°C)       | Time (min) | Cooling rate *1 (°C/s) |                                          | Temperature (°C) | Time (min) | Cooling         |
| 27  | Y             | 890                               | 800                        | 1          | 5                      | 50                                            | 900                    | 1          | 5                      | 60                                       | 660              | 480        | Furnace cooling |
| 28  | Y             | 890                               | 900                        | 1          | 5                      | 50                                            | 820                    | 1          | 5                      | 60                                       | 660              | 480        | Furnace cooling |
| 29  | Y             | 890                               | 800                        | 1          | 5                      | 50                                            | 830                    | 1          | 5                      | 60                                       | 660              | 480        | Furnace cooling |
| 30  | Y             | 890                               | 900                        | 1          | 1                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 31  | Y             | 890                               | 900                        | 1          | 10                     | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 32  | Y             | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 600              | 480        | Furnace cooling |
| 33  | Y             | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 550              | 480        | Air cooling     |
| 34  | Y             | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 530              | 480        | Air cooling     |
| 35  | Y             | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 40                                       | 660              | 480        | Furnace cooling |
| 36  | Y             | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 90                                       | 660              | 480        | Furnace cooling |
| 37  | Y             | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 700              | 480        | Furnace cooling |
| 38  | Y             | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 39  | Y             | 890                               | -                          | -          | -                      | 30                                            | 900                    | 1          | 5                      | 60                                       | 660              | 480        | Furnace cooling |
| 40  | Z             | 895                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |

(continued)

| No.                                                                                                                                               | Component No. | $\beta$ transformation point (°C) | Hot-rolled sheet annealing |            |                        | Intermediate cold rolling reduction ratio (%) | Intermediate annealing |            |                        | Rolling reduction in cold rolling *2 (%) | Final annealing  |            |                 |
|---------------------------------------------------------------------------------------------------------------------------------------------------|---------------|-----------------------------------|----------------------------|------------|------------------------|-----------------------------------------------|------------------------|------------|------------------------|------------------------------------------|------------------|------------|-----------------|
|                                                                                                                                                   |               |                                   | Temperature (°C)           | Time (min) | Cooling rate *1 (°C/s) |                                               | Temperature (°C)       | Time (min) | Cooling rate *1 (°C/s) |                                          | Temperature (°C) | Time (min) | Cooling         |
| 41                                                                                                                                                | <u>AA</u>     | 885                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 42                                                                                                                                                | <u>AB</u>     | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 43                                                                                                                                                | <u>AC</u>     | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 44                                                                                                                                                | <u>AD</u>     | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 45                                                                                                                                                | AE            | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 1440       | Furnace cooling |
| 46                                                                                                                                                | AF            | 880                               | 890                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 60         | Furnace cooling |
| 47                                                                                                                                                | AG            | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| 48                                                                                                                                                | AH            | 890                               | 900                        | 1          | 5                      | -                                             | -                      | -          | -                      | 60                                       | 660              | 480        | Furnace cooling |
| The underlines indicate that the results are out of the range of the present invention or out of the range of preferred manufacturing conditions. |               |                                   |                            |            |                        |                                               |                        |            |                        |                                          |                  |            |                 |
| *1: Cooling rates of hot-rolled sheet annealing and intermediate annealing are average cooling rates from annealing temperature to 700°C          |               |                                   |                            |            |                        |                                               |                        |            |                        |                                          |                  |            |                 |
| *2: Final cold rolling reduction ratio in case where intermediate annealing is performed                                                          |               |                                   |                            |            |                        |                                               |                        |            |                        |                                          |                  |            |                 |

[Table 3]

| No. | Component No. | $\alpha$ grain size             |                                                 |                                                 | Number of measurement regions containing 5 or more second phases among 100 measurement regions | Second phase (intermetallic compound) (%) | Room temperature     |                     | Tensile strength (800°C) (MPa) | Oxidation mass gain (mg/cm <sup>2</sup> ) | Glossiness Gs20 | Remarks             |
|-----|---------------|---------------------------------|-------------------------------------------------|-------------------------------------------------|------------------------------------------------------------------------------------------------|-------------------------------------------|----------------------|---------------------|--------------------------------|-------------------------------------------|-----------------|---------------------|
|     |               | Average value ( $\mu\text{m}$ ) | Proportion of average $\pm 2$ $\mu\text{m}$ (%) | Proportion of average $\pm 4$ $\mu\text{m}$ (%) |                                                                                                |                                           | Total elongation (%) | Erichsen value (mm) |                                |                                           |                 |                     |
| 1   | A             | 4.7                             | 57                                              | 87                                              | 88                                                                                             | 1.5                                       | 29.6                 | 10.2                | 29                             | 3.6                                       | 984             | Invention example   |
| 2   | B             | 4.5                             | 59                                              | 88                                              | 86                                                                                             | 1.6                                       | 28.3                 | 10.1                | 28                             | 3.5                                       | 978             | Invention example   |
| 3   | C             | 4.9                             | 56                                              | 86                                              | 83                                                                                             | 1.2                                       | 28.3                 | 9.7                 | 28                             | 3.6                                       | 977             | Invention example   |
| 4   | D             | 4.3                             | 60                                              | 91                                              | 86                                                                                             | 1.7                                       | 28.7                 | 10.2                | 28                             | 3.4                                       | 982             | Invention example   |
| 5   | E             | 4.8                             | 57                                              | 84                                              | 83                                                                                             | 1.2                                       | 28.8                 | 10                  | 27                             | 3.6                                       | 988             | Invention example   |
| 6   | F             | 4.1                             | 61                                              | 90                                              | 86                                                                                             | 1.3                                       | 29.1                 | 10.1                | 30                             | 3.7                                       | 996             | Invention example   |
| 7   | G             | 9.2                             | 30                                              | 51                                              | 81                                                                                             | 1.1                                       | 27.4                 | 10.2                | 28                             | 5.0                                       | 964             | Invention example   |
| 8   | H             | 4.0                             | 62                                              | 90                                              | 92                                                                                             | 2.8                                       | 28.1                 | 10                  | 31                             | 3.3                                       | 993             | Invention example   |
| 9   | I             | <u>198</u>                      | <u>18</u>                                       | <u>26</u>                                       | <u>63</u>                                                                                      | 0.3                                       | 40.1                 | 11.5                | 24                             | 6.7                                       | 882             | Comparative example |
| 10  | J             | 3.8                             | 60                                              | 90                                              | 90                                                                                             | 3.1                                       | 26.7                 | 9.3                 | 32                             | 3.3                                       | 975             | Comparative example |
| 11  | K             | 4.8                             | 55                                              | 83                                              | 86                                                                                             | 1.7                                       | 29.2                 | 9.8                 | 28                             | 3.6                                       | 967             | Invention example   |
| 12  | L             | 4.6                             | 53                                              | 81                                              | 85                                                                                             | 1.8                                       | 27.1                 | 10.1                | 29                             | 3.5                                       | 977             | Invention example   |

(continued)

| No. | Component No. | $\alpha$ grain size             |                                                 |                                                 | Number of measurement regions containing 5 or more second phases among 100 measurement regions | Second phase (intermetallic compound) (%) | Room temperature     |                     | Tensile strength (800°C) (MPa) | Oxidation mass gain (mg/cm <sup>2</sup> ) | Glossiness Gs20 | Remarks             |
|-----|---------------|---------------------------------|-------------------------------------------------|-------------------------------------------------|------------------------------------------------------------------------------------------------|-------------------------------------------|----------------------|---------------------|--------------------------------|-------------------------------------------|-----------------|---------------------|
|     |               | Average value ( $\mu\text{m}$ ) | Proportion of average $\pm 2$ $\mu\text{m}$ (%) | Proportion of average $\pm 4$ $\mu\text{m}$ (%) |                                                                                                |                                           | Total elongation (%) | Erichsen value (mm) |                                |                                           |                 |                     |
| 13  | M             | 4.3                             | 54                                              | 82                                              | 81                                                                                             | 1.8                                       | 28.5                 | 9.8                 | 34                             | 3.4                                       | 971             | Invention example   |
| 14  | N             | 4.2                             | 61                                              | 86                                              | 84                                                                                             | 1.9                                       | 27.6                 | 9.4                 | 35                             | 3.3                                       | 983             | Comparative example |
| 15  | O             | 4.1                             | 61                                              | 90                                              | 91                                                                                             | 2.1                                       | 26.9                 | 9.6                 | 30                             | 3.2                                       | 991             | Invention example   |
| 16  | P             | 2.5                             | 75                                              | 96                                              | 89                                                                                             | 2.2                                       | 23.7                 | 8.6                 | 28                             | 3.2                                       | 887             | Comparative example |
| 17  | Q             | 4.1                             | 63                                              | 88                                              | 83                                                                                             | 1.1                                       | 26.8                 | 9.6                 | 27                             | 3.9                                       | 988             | Invention example   |
| 18  | R             | 4.4                             | 53                                              | 84                                              | 84                                                                                             | 1.4                                       | 27.2                 | 9.7                 | 26                             | 6.4                                       | 969             | Comparative example |
| 19  | S             | 4.6                             | 54                                              | 82                                              | 82                                                                                             | 1.2                                       | 27.1                 | 9.6                 | 30                             | 3.4                                       | 974             | Invention example   |
| 20  | T             | 2.3                             | 73                                              | 94                                              | 89                                                                                             | 1.4                                       | 21.4                 | 8.4                 | 32                             | 5.8                                       | 897             | Comparative example |
| 21  | U             | 4.3                             | 56                                              | 89                                              | 88                                                                                             | 1.8                                       | 26.8                 | 9.7                 | 30                             | 3.4                                       | 988             | Invention example   |
| 22  | V             | 4.6                             | 56                                              | 86                                              | 86                                                                                             | 1.8                                       | 26.9                 | 9.6                 | 31                             | 3.2                                       | 983             | Invention example   |
| 23  | W             | 4.5                             | 55                                              | 87                                              | 82                                                                                             | 1.6                                       | 26.7                 | 9.6                 | 34                             | 3.2                                       | 979             | Invention example   |
| 24  | X             | 4.3                             | 52                                              | 90                                              | 92                                                                                             | 2.1                                       | 27.2                 | 9.8                 | 30                             | 3.3                                       | 984             | Invention example   |

(continued)

| No. | Component No. | $\alpha$ grain size             |                                                 |                                                 | Number of measurement regions containing 5 or more second phases among 100 measurement regions | Second phase (intermetallic compound) (%) | Room temperature     |                     | Tensile strength (800°C) (MPa) | Oxidation mass gain (mg/cm <sup>2</sup> ) | Glossiness Gs20 | Remarks             |
|-----|---------------|---------------------------------|-------------------------------------------------|-------------------------------------------------|------------------------------------------------------------------------------------------------|-------------------------------------------|----------------------|---------------------|--------------------------------|-------------------------------------------|-----------------|---------------------|
|     |               | Average value ( $\mu\text{m}$ ) | Proportion of average $\pm 2$ $\mu\text{m}$ (%) | Proportion of average $\pm 4$ $\mu\text{m}$ (%) |                                                                                                |                                           | Total elongation (%) | Erichsen value (mm) |                                |                                           |                 |                     |
| 25  | Y             | 4.5                             | 53                                              | 88                                              | 82                                                                                             | 1.4                                       | 29.8                 | 9.9                 | 27                             | 3.5                                       | 971             | Invention example   |
| 26  | Y             | 4.6                             | 58                                              | 86                                              | <u>78</u>                                                                                      | 1.3                                       | 27.9                 | 9.8                 | 28                             | 3.4                                       | 911             | Comparative example |
| 27  | Y             | 4.5                             | 58                                              | 86                                              | 84                                                                                             | 1.4                                       | 28.8                 | 9.6                 | 29                             | 3.6                                       | 992             | Invention example   |
| 28  | Y             | 4.7                             | 57                                              | 88                                              | 82                                                                                             | 1.5                                       | 29.6                 | 9.7                 | 28                             | 3.5                                       | 991             | Invention example   |
| 29  | Y             | 4.3                             | 54                                              | 81                                              | <u>78</u>                                                                                      | 1.3                                       | 28.7                 | 9.8                 | 28                             | 3.6                                       | 919             | Comparative example |
| 30  | Y             | 6.8                             | 31                                              | <u>44</u>                                       | 84                                                                                             | 1.4                                       | 28.2                 | 9.8                 | 28                             | 3.4                                       | 913             | Comparative example |
| 31  | Y             | 4.5                             | 58                                              | 86                                              | 82                                                                                             | 1.3                                       | 29.4                 | 9.7                 | 28                             | 3.3                                       | 986             | Invention example   |
| 32  | Y             | 3.8                             | 61                                              | 92                                              | 83                                                                                             | 1.4                                       | 29.3                 | 9.7                 | 28                             | 3.5                                       | 988             | Invention example   |
| 33  | Y             | 3.3                             | 60                                              | 95                                              | 82                                                                                             | 1.5                                       | 28.5                 | 9.6                 | 28                             | 3.5                                       | 978             | Invention example   |
| 34  | Y             | <u>2.4</u>                      | 72                                              | 94                                              | 82                                                                                             | 1.4                                       | 22.3                 | 8.7                 | 26                             | 3.4                                       | 876             | Comparative example |
| 35  | Y             | 8.9                             | <u>24</u>                                       | 49                                              | 82                                                                                             | 1.3                                       | 29.9                 | 9.8                 | 28                             | 3.5                                       | 900             | Comparative example |
| 36  | Y             | 4.6                             | 58                                              | 82                                              | 82                                                                                             | 1.4                                       | 30.1                 | 9.7                 | 27                             | 3.6                                       | 973             | Invention example   |

(continued)

| No. | Component No. | $\alpha$ grain size             |                                                 |                                                 | Number of measurement regions containing 5 or more second phases among 100 measurement regions | Second phase (intermetallic compound) (%) | Room temperature     |                     | Tensile strength (800°C) (MPa) | Oxidation mass gain (mg/cm <sup>2</sup> ) | Glossiness Gs20 | Remarks             |
|-----|---------------|---------------------------------|-------------------------------------------------|-------------------------------------------------|------------------------------------------------------------------------------------------------|-------------------------------------------|----------------------|---------------------|--------------------------------|-------------------------------------------|-----------------|---------------------|
|     |               | Average value ( $\mu\text{m}$ ) | Proportion of average $\pm 2$ $\mu\text{m}$ (%) | Proportion of average $\pm 4$ $\mu\text{m}$ (%) |                                                                                                |                                           | Total elongation (%) | Erichsen value (mm) |                                |                                           |                 |                     |
| 37  | Y             | <u>13.2</u>                     | 16                                              | <u>23</u>                                       | 61                                                                                             | 0.5                                       | 30.8                 | 10.6                | 28                             | 3.5                                       | 896             | Comparative example |
| 38  | Y             | 4.6                             | 54                                              | 88                                              | 82                                                                                             | 0.7                                       | 28.6                 | 9.9                 | 28                             | 3.7                                       | 956             | Invention example   |
| 39  | Y             | 5.3                             | 52                                              | 81                                              | 81                                                                                             | 0.9                                       | 28.1                 | 9.8                 | 29                             | 3.4                                       | 947             | Invention example   |
| 40  | <u>Z</u>      | 6.5                             | 47                                              | 71                                              | 83                                                                                             | 1.1                                       | 28.7                 | 10.9                | 25                             | 3.6                                       | 928             | Comparative example |
| 41  | <u>AA</u>     | 4.0                             | 58                                              | 91                                              | 84                                                                                             | 0.8                                       | 25.3                 | 9.1                 | 32                             | 3.6                                       | 943             | Comparative example |
| 42  | <u>AB</u>     | 7.5                             | 38                                              | 65                                              | 83                                                                                             | 0.9                                       | 29.4                 | 9.9                 | 25                             | 3.9                                       | 935             | Comparative example |
| 43  | <u>AC</u>     | 3.6                             | 62                                              | 94                                              | 81                                                                                             | 1.2                                       | 24.9                 | 9.2                 | 34                             | 3.8                                       | 963             | Comparative example |
| 44  | AD            | 5.5                             | 55                                              | 82                                              | 80                                                                                             | 1.1                                       | 28.7                 | 9.8                 | 27                             | 5.9                                       | 957             | Comparative example |
| 45  | AE            | 6.6                             | 35                                              | 77                                              | 88                                                                                             | 0.4                                       | 28.4                 | 9.6                 | 36                             | 4.8                                       | 955             | Invention example   |
| 46  | AF            | 5.7                             | 57                                              | 86                                              | 80                                                                                             | 0.2                                       | 27.9                 | 9.5                 | 26                             | 4.9                                       | 952             | Invention example   |
| 47  | AG            | 5.7                             | 51                                              | 85                                              | 82                                                                                             | 0.8                                       | 27.5                 | 9.6                 | 34                             | 4.2                                       | 944             | Invention example   |

(continued)

| No.                                                                                                                                               | Component No. | $\alpha$ grain size             |                                                 |                                                 | Number of measurement regions containing 5 or more second phases among 100 measurement regions | Second phase (intermetallic compound) (%) | Room temperature     |                     | Tensile strength (800°C) (MPa) | Oxidation mass gain (mg/cm <sup>2</sup> ) | Glossiness Gs20 | Remarks           |
|---------------------------------------------------------------------------------------------------------------------------------------------------|---------------|---------------------------------|-------------------------------------------------|-------------------------------------------------|------------------------------------------------------------------------------------------------|-------------------------------------------|----------------------|---------------------|--------------------------------|-------------------------------------------|-----------------|-------------------|
|                                                                                                                                                   |               | Average value ( $\mu\text{m}$ ) | Proportion of average $\pm 2$ $\mu\text{m}$ (%) | Proportion of average $\pm 4$ $\mu\text{m}$ (%) |                                                                                                |                                           | Total elongation (%) | Erichsen value (mm) |                                |                                           |                 |                   |
| 48                                                                                                                                                | AH            | 5.3                             | 52                                              | 88                                              | 81                                                                                             | 0.4                                       | 27.5                 | 9.7                 | 32                             | 3.7                                       | 959             | Invention example |
| The underlines indicate that the results are out of the range of the present invention or out of the range of preferred manufacturing conditions. |               |                                 |                                                 |                                                 |                                                                                                |                                           |                      |                     |                                |                                           |                 |                   |

**[0133]** As shown in Table 1, Nos. 1 to 8, 11 to 13, 15, 17, 19, 21 to 25, 27, 28, 31 to 33, 36, 38, 39, and 45 to 48 are titanium alloy sheets within the range of the present disclosure and exhibited excellent properties.

**[0134]** In addition, the form of the microstructure in all of these invention examples was an equiaxed structure. That is, the average aspect ratio (major axis length/minor axis length) of the  $\alpha$ -phase was 3.0 or less.

**[0135]** On the other hand, No. 9 had a low Si content and a coarse average crystal grain size of the  $\alpha$ -phase. In addition, the distribution state of the second phases also deteriorated. Accordingly, the oxidation mass gain was increased, and the oxidation resistance in a high-temperature environment was low. In addition, the high-temperature strength was also low. Furthermore, since the average crystal grain size of the  $\alpha$ -phase was large, the glossiness after polishing was low and the polishability was low.

**[0136]** In No. 10, the Si content was excessive, the Erichsen value was high, so the workability was low.

**[0137]** In No. 14, the Al content was excessive, the Erichsen value was high, so the workability was low.

**[0138]** In No. 16, the Zr content was excessive, the average crystal grain size of the  $\alpha$ -phase was small, and a large amount of non-recrystallized structure remained. For this reason, the total elongation was lowered and the Erichsen value was lowered, so the workability was lowered, and the polishability was also low.

**[0139]** In No. 18, the Cr content was excessive, and a  $\beta$ -phase was formed during high-temperature heating, resulting in low oxidation resistance.

**[0140]** In No. 20, the Mo content was excessive, the average crystal grain size of the  $\alpha$ -phase was small, and a large amount of non-recrystallized structure remained. For this reason, the total elongation and the Erichsen value were lowered, so the workability was lowered. In addition, the polishability was low. Furthermore, a  $\beta$ -phase was formed during high-temperature heating, resulting in low oxidation resistance.

**[0141]** In No. 26, since the annealing temperature of hot-rolled sheet annealing was below the  $\beta$  transformation point and no intermediate annealing was performed, the distribution state of the second phases deteriorated. As a result of observation, coarse crystal grains were included. As a result, the polishability was low.

**[0142]** In No. 29, since the annealing temperature of hot-rolled sheet annealing and the intermediate annealing temperature were below the  $\beta$  transformation point, the distribution state of the second phases deteriorated. As a result of observation, coarse crystal grains were included. As a result, the polishability was low.

**[0143]** In No. 30, since the cooling rate after hot-rolled sheet annealing was low and no intermediate annealing was performed, the distribution of the crystal grain size of the  $\alpha$ -phase was widened. As a result of observation, coarse crystal grains were included. As a result, the polishability was low.

**[0144]** In No. 34, the final annealing temperature was low, the average crystal grain size of the  $\alpha$ -phase was small, and a large amount of non-recrystallized structure remained. For this reason, the total elongation and the Erichsen value were lowered, so the workability was lowered. In addition, the polishability was low.

**[0145]** In No. 35, the rolling reduction of the final cold rolling was low and the introduction of strain was insufficient, so the distribution of the crystal grain size of the  $\alpha$ -phase was widened and coarse crystal grains were included, resulting in low polishability.

**[0146]** In No. 37, the final annealing temperature was high and the average grain size of the  $\alpha$  grains became coarse, and the distribution of the crystal grain size of the  $\alpha$ -phase was widened. In addition, the distribution of the second phases was not uniform. As a result, the polishability was low.

**[0147]** In No. 40, the Cu content was low, so the high-temperature strength was low.

**[0148]** In No. 41, the Cu content was excessive and the Erichsen value was high, so the workability was low.

**[0149]** In No. 42, the Sn content was low, so the high-temperature strength was low.

**[0150]** In No. 43, the Sn content was excessive and the total elongation and the Erichsen value were lowered, so the workability was low.

**[0151]** In No. 44, the Nb content was low, so the high-temperature oxidation resistance was low.

[Industrial Applicability]

**[0152]** According to the present disclosure, it is possible to provide a titanium alloy sheet and an exhaust system component for automobiles which have excellent workability, polishability, and high-temperature oxidation resistance.

## Claims

1. A titanium alloy sheet having a chemical composition of, by mass%,

Cu: 0.7% to 1.5%,

Sn: 0.5% to 1.5%,

Si: 0.10% to 0.60%,

Nb: 0.1% to 1.0%,

Zr: 0% to 1.0%,

Cr: 0% to 0.5%,

Mo: 0% to 0.5%,

Al: 0% to 1.0%,

Fe: limited to 0.08% or less,

O: limited to 0.07% or less, and

the balance of Ti and impurities,

wherein a microstructure consists of an  $\alpha$ -phase and second phases,

wherein an average crystal grain size of the  $\alpha$ -phase is 3.0 to 10.0  $\mu\text{m}$ ,

wherein, a number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 2 \mu\text{m}$  is 25% or higher in the  $\alpha$ -phase,

wherein, a number proportion of crystal grains having a crystal grain size within a range of the average crystal grain size  $\pm 4 \mu\text{m}$  is 45% or higher in the  $\alpha$ -phase, and

wherein, in a case where 100 of  $10 \mu\text{m} \times 10 \mu\text{m}$  regions obtained by dividing a  $100 \mu\text{m} \times 100 \mu\text{m}$  region into 100 equal parts in a cross section are set to measurement regions and a number density of the second phases is obtained for each measurement region, the number of measurement regions in which 5 to 15 second phases are observed within each measurement region is 80 or more.

2. The titanium alloy sheet according to claim 1,  
wherein the second phases have an area proportion of 1.0% or higher.

3. An exhaust system component for automobiles, comprising:  
the titanium alloy sheet according to claim 1 or 2.

4. An exhaust system component for automobiles which is obtained by forming the titanium alloy sheet according to claim 1 or 2.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2021/001778

## A. CLASSIFICATION OF SUBJECT MATTER

C22C 14/00 (2006.01) i; C22F 1/00 (2006.01) n; C22F 1/18 (2006.01) n  
 FI: C22C14/00 Z; C22F1/18 H; C22F1/00 623; C22F1/00 630K; C22F1/00 640B; C22F1/00 650A; C22F1/00 683; C22F1/00 684C; C22F1/00 685Z; C22F1/00 686A; C22F1/00 691B; C22F1/00 691C; C22F1/00 692A; C22F1/00 692B; C22F1/00 694A; C22F1/00 694B

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)

C22C14/00; C22F1/00; C22F1/18

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 | 1971-2021 |
| Registered utility model specifications of Japan         | 1996-2021 |
| Published registered utility model applications of Japan | 1994-2021 |

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. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
| A         | WO 2019/155553 A1 (NIPPON STEEL CORPORATION) 15 August 2019 (2019-08-15)           | 1-4                   |
| A         | WO 2011/081077 A1 (NIPPON STEEL CORP.) 07 July 2011 (2011-07-07)                   | 1-4                   |
| A         | JP 2005-298970 A (NIPPON STEEL CORP.) 27 October 2005 (2005-10-27)                 | 1-4                   |



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

"&amp;" document member of the same patent family

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 Tokyo 100-8915, Japan

Authorized officer

Telephone No.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2021/001778

| Patent Documents<br>referred in the<br>Report | Publication<br>Date | Patent Family                                                                                                                               | Publication<br>Date |
|-----------------------------------------------|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------|---------------------|
| WO 2019/155553 A1                             | 15 Aug. 2019        | US 2020/0347484 A1<br>EP 3712282 A1<br>KR 10-2020-0112940 A<br>CN 111655880 A                                                               |                     |
| WO 2011/081077 A1                             | 07 Jul. 2011        | US 2012/0267001 A1<br>US 2018/0195154 A1<br>EP 2520677 A1<br>KR 10-2012-0063552 A<br>CN 102666892 A                                         |                     |
| JP 2005-298970 A                              | 27 Oct. 2005        | US 2007/0187008 A1<br>US 2011/0132500 A1<br>US 2012/0148437 A1<br>US 2014/0348697 A1<br>WO 2005/090623 A1<br>EP 1726670 A1<br>EP 2333130 A1 |                     |

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 2007270199 A [0012]
- JP 2005290548 A [0012]
- JP 2009030140 A [0012]
- JP 2013142183 A [0012]