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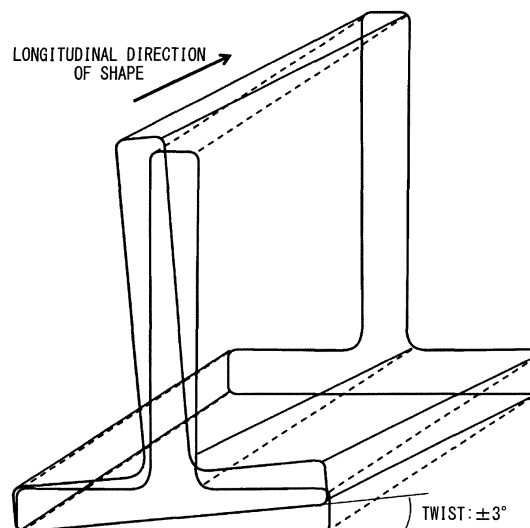
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(54) **$\alpha+\beta$ TYPE TITANIUM ALLOY SHAPED MATERIAL AND MANUFACTURING METHOD THEREOF**

(57) An $\alpha+\beta$ titanium alloy shape according to an aspect of the present invention has an acicular microstructure, wherein a 0.2% proof stress is 830 MPa or more, an elongation is 10% or more, and a fatigue

strength is 450 MPa or more, an area fraction of voids is $1.0 \times 10^{-5}\%$ or less, a twist angle from one end to the other end is within $\pm 3.0^\circ$, and a warpage height (mm)/total length (m) is within ± 2.17 .

FIG. 5



EP 4 459 000 A1

Description

[Technical Field of the Invention]

5 **[0001]** The present invention relates to an $\alpha+\beta$ titanium alloy shape and a method for manufacturing the same.

[Related Art]

10 **[0002]** Titanium alloys have been applied to parts such as connecting rods and mufflers of automobiles, and consumer products such as golf face club heads and building materials by taking advantage of high specific strength and excellent corrosion resistance. In addition, titanium alloys are compatible with a living body, thus are also widely used in decorative articles such as watches and eyeglass frames, medical applications such as implants, and the like.

15 **[0003]** Titanium alloys are classified into three: α alloys, β alloys, and $\alpha+\beta$ alloys. The α titanium alloy is a titanium alloy whose metallographic structure at room temperature is mainly composed of α phase, the β titanium alloy is a titanium alloy whose metallographic structure at room temperature is mainly composed of β phase, and the $\alpha+\beta$ titanium alloy is a titanium alloy whose metallographic structure at room temperature is composed of both α phase and β phase. The α phase of the titanium alloy is a phase with a hexagonal close-packed structure (hcp), and the β phase of the titanium alloy is a phase with a body-centered cubic structure (bcc).

20 **[0004]** In pure titanium, all the metallographic structures at room temperature are α phase, and all the metallographic structures at a temperature exceeding β transus temperature are β phase. However, by adding an alloying element for stabilizing the β phase to pure titanium, the temperature at which the β phase can be stably present is lowered, and the β phase remains even at room temperature. The temperature region exceeding the β transus temperature, in which the metallographic structure becomes a β single phase, is referred to as a β single-phase temperature region. In addition, the temperature region below the β transus temperature, in which the metallographic structure includes both α phase and β phase, is referred to as an $\alpha+\beta$ two-phase temperature region.

25 **[0005]** Among titanium alloys, the $\alpha+\beta$ titanium alloy has been used for a long time since it has excellent strength-ductility balance and fatigue properties. As one of applications of the $\alpha+\beta$ titanium alloy, fuel consumption reduction by weight reduction in the fields of automobiles and two-wheeled vehicles has recently attracted attention. Although the weight of the $\alpha+\beta$ titanium alloy is about 60% of that of carbon steel or stainless steel, the $\alpha+\beta$ titanium alloy has substantially the same strength and fatigue properties as those of carbon steel and stainless steel. Therefore, by replacing a crankshaft or an engine component formed of carbon steel or stainless steel with one formed of the $\alpha+\beta$ titanium alloy, the weight of the entire engine can be reduced, the output can be improved, and the fuel consumption can be reduced.

30 **[0006]** Generally, materials of crankshafts, and engine components such as valves and connecting rods are hot worked products such as round bars, billets, square bars, and wrought materials supplied in a form with a uniform cross section. Hereinafter, these materials are collectively referred to as "shape". That is, the "shape" means a wrought material which has a uniform cross section over the total length and is supplied in a linear form. In a stage where the shape is manufactured by means such as extrusion and rolling, the shape has bend or twist, and thus is usually removed by means such as straightening and annealing. The shape of the $\alpha+\beta$ titanium alloy can be applied to the above-mentioned wide region of applications by cutting, further working, cutting after further working, or the like.

40 **[0007]** The $\alpha+\beta$ titanium alloy can achieve excellent strength-ductility balance and fatigue properties by performing strong working in an $\alpha+\beta$ two-phase temperature region equal to or lower than the β transus temperature to control the metallographic structure to an equiaxed grain microstructure. Conventionally, a shape with a complicated form has been manufactured by cutting a forged product or a thick plate manufactured by strong working in an $\alpha+\beta$ two-phase temperature region.

45 **[0008]** However, since cutting increases the manufacturing cost of the machine parts, it is preferable to reduce the amount as much as possible. At present, in order to reduce the manufacturing cost, a manufacturing technology capable of improving the production efficiency by manufacturing a long shape with a cross-sectional form closer to the final product is being developed. By using a shape with a cross section close to the final product as a material, the cutting amount can be reduced and the yield can be improved. In addition, productivity can be improved by increasing the length of the shape.

50 **[0009]** For example, an ingot or a round billet obtained by hot forging an ingot is used as a material in Ugine-Sejourmet process which is one of extrusion processing methods. As shown in FIG. 1, a material (a billet 5) is inserted into a container 1, a load by hydraulic pressure is applied to a stem 2 to press the billet 5 in an extrusion direction 11 via a dummy block 3, and the billet 5 is passed through a die 4 to be formed into various cross-sectional forms, whereby a long shape 6 can be obtained.

55 **[0010]** In working into such a complicated form, the hot deformation resistance of the $\alpha+\beta$ titanium alloy rapidly increases in a temperature region below the β transus temperature. Therefore, in order to work the $\alpha+\beta$ titanium alloy in the temperature region below the β transus temperature and control the microstructure to an equiaxed microstructure, a large facility capable of applying a high load is required. This increases the equipment cost. In addition, depending on the

required cross-sectional form, it may be impossible to hot work the $\alpha+\beta$ titanium alloy in the temperature region below the β transus temperature. Furthermore, even in a case where working is possible, when the temperature of a part in the cross section of the shape exceeds the β transus temperature due to working heat generation, an equiaxed microstructure and an acicular microstructure obtained by working at a temperature equal to or higher than the β transus temperature are mixed in the cross section of the shape, and a significant difference in mechanical properties occurs in the cross section. Therefore, in general, when an $\alpha+\beta$ titanium alloy is hot worked into a complicated form, the $\alpha+\beta$ titanium alloy can be manufactured with low hot deformation resistance, and is worked at a temperature equal to or higher than the β transus temperature at which surface defects are less likely to occur, and forced cooling is performed as necessary, so that the metallographic structure is controlled to a fine acicular microstructure, and the required excellent strength-ductility balance and fatigue properties have been realized.

[0011] A problem here is that, in general, bend and twist occur in a hot worked shape. The bend and twist are caused by remaining of a processing strain in the shape and the non-uniform cooling rate of the shape for each portion. Therefore, in the manufacture of the shape, further straightening working is required after the hot working described above.

[0012] The straightening method includes roll straightening and tension straightening. The roll straightening is a method of passing the shape between a plurality of rolls to undergo bending deformation and unbending deformation, thereby improving bend and twist of the shape. The tension straightening is a method of fixing both ends of the shape and applying a tensile load to deform the shape to a plastic deformation region, thereby improving bend and twist of the shape.

[0013] Since the $\alpha+\beta$ titanium alloy has large cold deformation resistance, straightening working is also generally performed hot. In the shape of the $\alpha+\beta$ titanium alloy with an acicular microstructure, by hot straightening, straightening can be performed with a lower load than at room temperature. In addition, since the $\alpha+\beta$ titanium alloy has a narrow elastic region at a high temperature as compared with that at room temperature, the $\alpha+\beta$ titanium alloy can be straightened with a slight amount of deformation. Furthermore, in the $\alpha+\beta$ titanium alloy, at a high temperature, the soft β phase fraction is higher than that at room temperature, and the strain is easily recovered.

[0014] However, when the $\alpha+\beta$ titanium alloy shape is straightened so that the deformation amount increases in a low temperature region of the $\alpha+\beta$ two-phase temperature region, a large number of coarse voids, which are internal defects, are formed. As a result, there has been a problem that excellent strength-ductility balance and fatigue properties required for the shape cannot be realized. Furthermore, the $\alpha+\beta$ titanium alloy has a low Young's modulus. Therefore, when the $\alpha+\beta$ titanium alloy is hot straightened, large spring back occurs after cooling to room temperature, and twist is not sufficiently improved in many cases.

[0015] For the above reasons, in the $\alpha+\beta$ titanium alloy shape that requires form straightening, it has not been always possible to achieve the required excellent strength-ductility balance, fatigue properties, and excellent form at the same time.

[0016] Patent Document 1 discloses a method for straightening an $\alpha+\beta$ titanium alloy in which a billet, a square bar, a tube, or the like that has been age-hardened is straightened by applying a tensile stress at a temperature of about 0.3 times (about 480°C) the melting temperature, and further cooled while applying the tensile stress.

[0017] Patent Document 2 discloses a method for straightening an $\alpha+\beta$ titanium alloy in which a rolled titanium alloy round bar is annealed for microstructure adjustment, and then bending straightening by press straightening and warm straightening at 600°C to β transus temperature are performed.

[Citation List]

[Patent Document]

[0018]

[Patent Document 1]

Japanese Patent No. 6058535

[Patent Document 2]

Japanese Unexamined Patent Application, First Publication No. 2011-137204

[Summary of Invention]

[Problems to be Solved by the Invention]

[0019] In the hot straightening of a general $\alpha+\beta$ titanium alloy, a method of straightening by 2 to 3% in a high temperature region (about 700 to 740°C), holding the alloy for about 10 to 30 minutes in a high temperature region also for annealing while maintaining the length of the alloy, then unloading the alloy, cooling the alloy to about 400 to 600°C, removing the alloy from a straightener, and cooling the alloy is performed. When the shape has a circular form, the cooling rate inside the cross

section is uniform, so that the difference in thermal shrinkage is small, and warpage hardly occurs during air cooling after straightening.

[0020] However, when the shape has a square form or a complicated form close to a product form, the temperature difference in the cross section during heating and/or before air cooling increases due to, for example, the presence of corner portion with a high cooling rate or the difference in sheet thickness and the difference in thermal shrinkage also increases. As a result, warpage occurs in the shape after being detached from the straightener and cooled, or there is a problem that the residual stress inside the shape is large and warpage occurs when the shape is cut after cooling even though no warpage occur after cooling. FIG. 2 shows an example (a) of a shape with a conventional simple form and an example (b) of a shape with a cross-sectional form closer to a product form of the $\alpha+\beta$ titanium alloy shape. FIG. 2 is a cross-sectional view, and the shape extends from the front to the back of the paper.

[0021] In addition, FIGS. 3 to 6B show schematic views relating to a form that becomes a problem in a shape and a form change in cutting. FIG. 3 are examples of cross-sectional forms of hot straightened shapes. FIG. 4 is an example of warpage in a shape. FIG. 5 is an example of twist in a shape. FIGS. 6A and 6B are examples of dimensional changes after cutting. Note that the warpage in FIG. 4 and the twist in FIG. 5 need to be within a limit value of $\pm$ in the vertical direction on the paper, and the dimensional changes in FIGS. 6A and 6B need to be within a limit value of $\pm$ in the horizontal direction on the paper.

[0022] In Patent Document 1, a titanium alloy is subjected to an $\alpha+\beta$ two-phase region heat treatment, and then a tensile stress is applied during cooling, so that stress generated during cooling is balanced, and pure titanium and a titanium alloy product are straightened. However, in this technique, the tensile stress applied to the shape for straightening is at least 20% of the yield stress of the shape at the straightening temperature. When such a large tensile stress is applied to a shape with an acicular microstructure, stress concentrates at a portion where twist or bend is large, and a void may be generated inside. In addition, since the titanium alloy described in Patent Document 1 is rolled at the $\alpha+\beta$ two-phase temperature region, it is estimated that the microstructure is composed of not an acicular microstructure but mainly an equiaxed grains.

[0023] In Patent Document 2, a titanium alloy round bar is annealed for microstructure adjustment, and then surface polishing is performed after final straightening by bending straightening by press straightening, cutting and removing of surface defects, and warm straightening at 600°C to β transus temperature, thereby manufacturing a titanium alloy round bar product. However, in the roll straightening, since the transport time from a heating device to a roll straightener is different in the longitudinal direction, a cross-sectional dimensional difference occurs in the longitudinal direction, and productivity and overall yield are lowered.

[0024] As a means for reducing warpage, a method of straightening at a low temperature at which a temperature difference is small in the cross section, can be considered. However, since the elastic limit is large at a low temperature, a very large strain is required for eliminating twist. In addition, since stress concentration occurs at the β grain boundary under tensile stress in the $\alpha+\beta$ titanium alloy with an acicular microstructure, a void is generated inside the alloy which can be a starting point of fatigue fracture and fatigue properties are significantly deteriorated, and strength-ductility balance is also deteriorated. That is, many problems remain in the conventional method in order to manufacture the $\alpha+\beta$ titanium alloy shape in a complicated form closer to a product form.

[0025] In view of the above circumstances, an object of the present invention is to provide an $\alpha+\beta$ titanium alloy shape with less warpage and twist and excellent proof stress, fatigue strength, and ductility, and a method for manufacturing the same.

[Means for Solving the Problem]

[0026] The gist of the present invention is as follows.

(1) An $\alpha+\beta$ titanium alloy shape according to an aspect of the present invention includes an acicular microstructure, wherein a 0.2% proof stress is 830 MPa or more, an elongation is 10.0% or more, a fatigue strength is 450 MPa or more, an area fraction of voids is $1.0 \times 10^{-5}\%$ or less, a twist angle from one end to the other end is within $\pm 3.0^\circ$, and a warpage height (mm)/total length (m) is within ± 2.17 .

(2) It is preferable that, in the $\alpha+\beta$ titanium alloy shape according to (1) above, the 0.2% proof stress is 850 MPa or more.

(3) It is preferable that, in the $\alpha+\beta$ titanium alloy shape according to (1) or (2) above, the area fraction of voids is $1.0 \times 10^{-6}\%$ or less.

(4) It is preferable that, in the $\alpha+\beta$ titanium alloy shape according to any one of (1) to (3) above, the average prior β grain size is 500 μm or less.

(5) It is preferable that, in the $\alpha+\beta$ titanium alloy shape according to any one of (1) to (4) above, the maximum residual stress in the cross section is +400 MPa or less.

(6) It is preferable that the $\alpha+\beta$ titanium alloy shape according to any one of (1) to (5) above is an extruded shape.

(7) It is preferable that the $\alpha+\beta$ titanium alloy shape according to any one of (1) to (6) above contains, in mass%, Al: 4.4

to 6.5%, Fe: 0.5 to 2.9%, Si: 0 to 0.50%, O: 0 to 0.25%, C: 0 to 0.08%, N: 0 to 0.05%, Ni: 0 to 0.15%, Cr: 0 to 0.25%, and Mn: 0 to 0.25%, with the remainder being Ti and impurities, and the contents of Fe, Ni, Cr, and Mn, %Fe, %Ni, %Cr, and %Mn, expressed in mass%, satisfy $0.5\% \leq \%Fe + \%Ni + \%Cr + \%Mn \leq 2.9\%$.

(8) It is preferable that the $\alpha+\beta$ titanium alloy shape according to any one of (1) to (6) above contains, in mass%, Al: 4.4 to 5.5%, Fe: 1.4 to 2.3%, Mo: 1.5 to 5.5, O: 0 to 0.20%, C: 0 to 0.08%, N: 0 to 0.05%, Si: 0 to 0.10%, Ni: 0 to 0.15%, Cr: 0 to 0.25%, and Mn: 0 to 0.25%, with the remainder being Ti and impurities, and the contents of Fe, Ni, Cr, and Mn, %Fe, %Ni, %Cr, and %Mn, expressed in mass%, satisfy $1.4\% \leq \%Fe + \%Ni + \%Cr + \%Mn \leq 2.3\%$.

(9) A method for manufacturing an $\alpha+\beta$ titanium alloy shape according to another aspect of the present invention is a method for manufacturing the $\alpha+\beta$ titanium alloy shape according to any one of (1) to (8) above including: hot working an $\alpha+\beta$ titanium alloy to obtain a shape; heating the shape to a straightening temperature of equal to or higher than β transus temperature - 400°C and equal to or lower than β transus temperature - 200°C, applying a strain of 0.1% or more and 8% or less in a longitudinal direction at the straightening temperature, and further applying a torque that makes a twist in the longitudinal direction of the shape within $\pm 3.0\%$; and cooling the shape to 500°C or lower while applying tensile stress and the torque to the shape.

(10) It is preferable that, in the method for manufacturing an $\alpha+\beta$ titanium alloy shape according to (9) above, the tensile stress applied during cooling of the shape is 20% or less of 0.2% proof stress at room temperature.

(11) It is preferable that the method for manufacturing an $\alpha+\beta$ titanium alloy shape according to (9) or (10) above further includes holding the shape at 500 to 650°C during cooling of the shape.

(12) It is preferable that, in the method for manufacturing an $\alpha+\beta$ titanium alloy shape according to any one of (9) to (11) above, an average cooling rate of the shape from the straightening temperature to 500°C is 10°C/s or less.

[Effects of the Invention]

[0027] According to the present invention, it is possible to provide an $\alpha+\beta$ titanium alloy shape with less warpage and twist and excellent proof stress, fatigue strength, and ductility, and a method for manufacturing the same.

[Brief Description of the Drawings]

[0028]

FIG. 1 is a diagram showing Ugine-Sejournet process.

FIG. 2 are examples of cross-sectional forms of $\alpha+\beta$ titanium alloy shapes, in which FIG. 2(a) is an example of a shape with a simple form, and FIG. 2(b) is an example of a shape closer to a product form.

FIG. 3 are examples of cross-sectional forms of hot straightened shapes.

FIG. 4 is an example of warpage in a shape.

FIG. 5 is an example of twist in a shape.

FIG. 6A is an example of dimensional variation after cutting in a shape with a T-formed cross section.

FIG. 6B is an example of dimensional variation after cutting in a shape with a U-formed cross section.

FIG. 7A are micrographs of an example of an acicular microstructure.

FIG. 7B are micrographs of an example of an equiaxed microstructure.

FIG. 8 are examples of voids contained in an $\alpha+\beta$ titanium alloy shape.

FIG. 9A is an example of a cross-sectional form of an $\alpha+\beta$ titanium alloy shape.

FIG. 9B is an example of a cross-sectional form of an $\alpha+\beta$ titanium alloy shape.

FIG. 9C is an example of a cross-sectional form of an $\alpha+\beta$ titanium alloy shape.

[Embodiments of the Invention]

[0029] The present inventors have extensively conducted studies on a method for obtaining an $\alpha+\beta$ titanium alloy shape with less warpage and twist and excellent proof stress, fatigue strength, and ductility. As a result, it has been clarified that the above-described problems are solved by straightening the $\alpha+\beta$ titanium alloy shape under predetermined heating conditions and stress conditions and then subsequently cooling the shape to a low temperature while applying a tensile load.

[0030] Conventionally, when warpage or twist had not been eliminated even by straightening working, a portion including warpage or twist has been discarded, which has reduced the manufacturing yield of machine parts. Therefore, when the warpage and twist have been eliminated, effects such as improvement of the manufacturing yield of machine parts and cost reduction can be obtained.

[0031] Hereinafter, an $\alpha+\beta$ titanium alloy shape according to an aspect of the present invention will be described in detail.

[0032] The $\alpha+\beta$ titanium alloy shape according to the present embodiment has excellent strength-ductility balance and

fatigue strength. Furthermore, even in the case of a complicated form close to a product, the shape has an excellent form. Specifically, the $\alpha+\beta$ titanium alloy shape according to the present embodiment has a 0.2% proof stress of 830 MPa or more, preferably 840 MPa or more, and 850 MPa or more, a total elongation of 10.0% or more, preferably 10.3% or more, preferably 12.0% or more, and a fatigue strength of 450 MPa or more, and preferably 480 MPa or more. The upper limit of 0.2% proof stress is not particularly limited, but for example, the 0.2% proof stress may be 1400 MPa or less, 1300 MPa or less, or 1200 MPa or less. The upper limit of the total elongation is also not particularly limited, but for example, may be 30% or less, 28% or less, or 25% or less. The upper limit of the fatigue strength is also not particularly limited, but for example, may be a fatigue strength of 800 MPa or less, 750 MPa or less, or 700 MPa or less. Such mechanical properties can be achieved, for example, by a manufacturing method described later. In the following description, the "total elongation" may be simply referred to as "elongation".

[0033] The shape according to the present embodiment is a so-called $\alpha+\beta$ titanium alloy. The $\alpha+\beta$ titanium alloy includes α phase with an HCP structure and β phase with a BCC structure at a temperature equal to or lower than the β transus temperature. In addition, the $\alpha+\beta$ titanium alloy includes only the β phase by transformation of α phase to β phase at a temperature equal to or higher than the β transus temperature.

[0034] Further, the $\alpha+\beta$ titanium alloy shape according to the present embodiment has an acicular microstructure. The acicular microstructure is a microstructural morphology generated when the $\alpha+\beta$ titanium alloy is cooled from a temperature equal to or higher than the β transus temperature. As exemplified in FIG. 7A, in the acicular microstructure, a grain boundary α phase is formed at a prior β grain boundary, and a microstructure in which α phase and β phase are arranged in layers in the prior β grain is formed. Here, the prior β grain boundary is a trace of the grain boundary of the β phase present at a temperature equal to or higher than the β transus temperature. When the $\alpha+\beta$ titanium alloy in a temperature region equal to or higher than the β transus temperature is cooled, the α phase preferentially precipitates at the grain boundary of the prior β phase, and this becomes the grain boundary α phase.

[0035] The $\alpha+\beta$ titanium alloy shape according to the present embodiment may include only an acicular microstructure, or may have both an acicular microstructure and an equiaxed microstructure. The equiaxed microstructure is a microstructure that does not have the characteristics of the acicular microstructure described above, and includes, for example, α grains and a transformed β phase as exemplified in FIG. 7B. Here, the transformed β phase is a layered microstructure of β phase and α phase, and is a microstructure that is β phase during hot working and is phase-transformed into β phase and α phase during cooling after hot working.

[0036] In the $\alpha+\beta$ titanium alloy with an acicular microstructure, voids are likely to be generated at the prior β grain boundary under tensile stress. In general, it is considered that the vicinity of voids inside the metal has a high stress concentration coefficient under tensile stress, tends to be a starting point of fracture during a tensile test or a fatigue test, elongation decreases, and 0.2% proof stress and the fatigue strength also decrease.

[0037] In the conventional straightening technique, tension straightening or roll straightening is performed in a high temperature region of an $\alpha+\beta$ two-phase temperature region of a narrow elastic region so as not to generate voids, and then air cooling is performed, or cooling is performed by fixing with a die in order to suppress deformation due to thermal stress during cooling. As a result, both material properties and dimensional accuracy are obtained. However, when the shape has an end portion with a high cooling rate or when the shape has a complicated form, a temperature difference in the cross section during heating increases due to, for example, a difference in cooling rate or sheet thickness, and at the same time, a difference in thermal shrinkage during cooling also increases. For this reason, during cooling in the straightening working, a significant stress is generated inside the shape, which give plastic deformation such as warpage or twist to the shape. In addition, even when plastic deformation does not occur during cooling in the straightening working and when plastic deformation is suppressed by the die, residual stress is generated inside the shape which gives a form defect such as warpage in cutting work of the shape.

[0038] In the $\alpha+\beta$ titanium alloy shape according to the present embodiment, the average value of the grain sizes in the region surrounded by the prior β grain boundary, that is, the average prior β grain size is not particularly limited, but is preferably, for example, 500 μm or less. This further enhances the mechanical properties of the shape. When the shape is manufactured by hot rolling and then straightened, the average prior β grain size is usually more than 500 μm . Hot rolling is usually performed in multiple passes using a hot rolling apparatus, and β grains grow as the titanium alloy moves between these passes. In addition, since the amount of strain per pass introduced during hot rolling is small, strain is recovered when the titanium alloy moves between these passes, and recrystallization is less likely to occur. For these reasons, the average prior β grain size of the titanium alloy shape obtained by hot rolling is coarsened. On the other hand, for example, when a shape is formed by hot extrusion and then straightened, the average prior β grain size is 500 μm or less. The average prior β grain size may be 450 μm or less, 400 μm or less, or 350 μm or less. The lower limit of the average prior β grain size is not particularly limited, but for example, the average prior β grain size may be 50 μm or more, or 80 μm or more. Since the cross section of the shape cannot be formed into a complicated form by hot rolling, the $\alpha+\beta$ titanium alloy shape according to the present embodiment is preferably an extruded shape manufactured by hot extrusion.

[0039] The method for measuring the average prior β grain size is as follows. First, a test piece for microstructure observation is collected from the inside of the shape. The test piece does not include a region from the surface of the shape

to a depth of 0.5 mm. Then, the test piece is wet polished and buff polished to bring the polished surface into a mirror surface state. The polished surface is corroded using fluonitric acid to exhibit a metallographic structure. When the corroded surface is observed with an optical microscope, a grain boundary α phase as shown in FIG. 7A can be identified. The grain boundary α phase can be regarded as a prior β grain boundary. The average value of the prior β grain size can be obtained by measuring the circle equivalent diameter of the portion surrounded by the prior β grain boundary by a cutting method. When the grain size is measured by the cutting method, the size of the measurement region is set to 7 mm square, the measurement magnification is set to 50 to 200 times, and 15 vertical straight lines and 15 horizontal straight lines are drawn at equal intervals in the measurement region.

[0040] In the $\alpha+\beta$ titanium alloy shape according to the present embodiment, an area fraction of voids is $1.0 \times 10^{-5}\%$ or less, and the microstructure is an acicular microstructure. As a result, a high strength-ductility balance and fatigue properties are obtained. The fact that the microstructure is an acicular microstructure means that 50% or more of the microstructure in terms of area fraction is an acicular microstructure, and preferably 60% or more, more preferably 70% or more, and most preferably 100% is an acicular microstructure. The microstructure other than the acicular microstructure is an equiaxed microstructure. Also, the area fraction of voids is preferably $5.0 \times 10^{-6}\%$ or less, $1.0 \times 10^{-6}\%$ or less, or $1.0 \times 10^{-7}\%$ or less. As described above, the void can be a starting point of fatigue fracture, and significantly deteriorates fatigue properties. Furthermore, voids also adversely affect strength and ductility. Therefore, the area fraction of voids is preferably as small as possible. The lower limit of the area fraction of voids is not particularly limited, and may be, for example, 0%. The area fraction of voids may be defined as $1.0 \times 10^{-9}\%$ or more, $5.0 \times 10^{-9}\%$ or more, or $1.0 \times 10^{-8}\%$ or more.

[0041] The acicular microstructure and the equiaxed microstructure will be described in detail below. The acicular microstructure is, for example, as shown in FIG. 7A, a microstructure composed of a microstructure in which α phase and β phase are arranged in layers and a thin grain boundary α phase surrounding the microstructure. The equiaxed microstructure is, for example, as shown in FIG. 7B, a microstructure composed of a granular pro-eutectoid α phase, a transformed β phase not surrounded by a grain boundary α phase, or the like. When the $\alpha+\beta$ titanium alloy is naturally cooled without being machined after being heated to the β temperature region, the microstructure mainly becomes an acicular microstructure. On the other hand, when the $\alpha+\beta$ titanium alloy is hot worked in the $\alpha+\beta$ two-phase temperature region and then cooled, an equiaxed microstructure is generated. The amounts of acicular microstructures and equiaxed microstructures vary depending on the temperature of hot working, the amount of strain applied, and the like.

[0042] The method for measuring the amount of acicular microstructure is as follows. First, a test piece for microstructure observation is collected from the inside of the shape. The test piece does not include a region from the surface of the shape to a depth of 0.5 mm. Then, the test piece is polished, and the polished surface is corroded using fluonitric acid to exhibit a metallographic structure. When the corroded surface is observed with an optical microscope, a grain boundary α phase as shown in FIG. 7A can be identified. The ratio of the area fraction of the region surrounded by the grain boundary α and the grain boundary α phase included in the measurement visual field to the entire area of the measurement visual field is regarded as the area fraction of the acicular microstructure of the shape.

[0043] The voids are observed using an optical microscope after mirror polishing a sample collected from the cross section and longitudinal cross section of the shape. The sample does not include a region from the surface of the shape to a depth of 0.5 mm. The void is the total area of voids having an equivalent circle diameter of $1 \mu\text{m}$ or more in terms of area. When observed with an optical microscope, the void can be visually recognized as a circular dark region, for example, as shown in FIG. 8.

[0044] The residual stress is measured by a 2D method using an X-ray diffraction method (Bruker AXS D8 Discover). The tube is Cu, the collimator diameter is 2.0 mm, the measurement diffraction line is (302) of the Ti α phase, the cross section of the center portion of the length of the shape is mirror-polished, the residual stress distribution in the in-plane cross sectional direction is measured, and the residual stress value at which the absolute value is maximized is obtained. The cross section is a cross section perpendicular to the length direction of the shape.

[0045] A specific example for measuring the absolute maximum value of the residual stress will be described below. For example, in the case of a shape with a T-formed cross section including a horizontal plate and a vertical plate abutting against the center of the horizontal plate as shown in FIG. 6A, the residual stress is maximized at any position of the central axis of the vertical plate. Therefore, the maximum residual stress in the cross section of the shape is obtained by measuring the residual stress along the central axis of the vertical plate.

[0046] The $\alpha+\beta$ titanium alloy shape after hot straightening according to the present embodiment preferably has a small dimensional change when subjected to cutting. Regarding the dimensional change during the cutting, it was determined that there is no problem in working into parts and products as long as the dimensional change is within ± 2.0 mm in the cross section. The dimensional change during the cutting is preferably within ± 1.5 mm, and further preferably within ± 1.0 mm. It is needless to say that the dimensional change is preferably small.

[0047] This dimensional change is caused by residual stress inside the shape. In order that the dimensional change in the cross section during the cutting is within ± 2.0 mm, the maximum residual stress in the cross section is preferably +400 MPa or less, and more preferably +300 MPa or less. Note that it is estimated that the residual stress, which is the main

cause of the dimensional change during the cutting, decreases in the absolute value of the residual stress, thereby also decreasing the dimensional change during the cutting.

[0048] The chemical composition of the titanium alloy according to the present embodiment is not particularly limited as long as it is components of the $\alpha+\beta$ titanium alloy as exemplified above, and for example, the chemical composition can be components like (1) and (2) below. Hereinafter, "%" represents "mass%".

(1) Al: 4.4 to 6.5%, Fe: 0.5 to 2.9%, Si: 0 to 0.50%, O: 0 to 0.25%, C: 0 to 0.080%, N: 0 to 0.050%, Ni: 0 to 0.15%, Cr: 0 to 0.25%, Mn: 0 to 0.25%, remainder: Ti, and impurities in a total amount of 0.4% or less, and the contents of Fe, Ni, Cr, and Mn, %Fe, %Ni, %Cr, and %Mn, expressed in mass%, satisfy $1.4\% \leq \%Fe + \%Ni + \%Cr + \%Mn \leq 2.9\%$.

Al: 4.4 to 6.5%

[0049] Al is an α -stabilizing element and may be contained in order to increase the fraction of the α phase. In consideration of the balance among 0.2% proof stress, ductility, and toughness, the amount of Al is preferably 4.4 to 6.5%.

Fe: 0.5 to 2.9%

[0050] Fe is a β -stabilizing element, and has an action of lowering the β transus temperature by being contained in the titanium alloy. In addition, Fe has an action of improving 0.2% proof stress. The amount of Fe is preferably 0.5 to 2.9% in consideration of the balance between 0.2% proof stress and segregation during solidification and elongation.

Si: 0 to 0.50%, O: 0 to 0.25%, C: 0 to 0.080%, N: 0 to 0.050%

[0051] Si, O, C, and N are not necessarily contained, and the lower limit of the content is 0. These elements are also elements having the same effect as the α -stabilizing element, and have an action of increasing the fraction of the α phase and improving 0.2% proof stress by being contained in the titanium alloy. In consideration of the balance with ductility, the contents are preferably Si: 0 to 0.50%, O: 0 to 0.25%, C: 0 to 0.080%, and N: 0 to 0.050%. However, when the contents of these elements are 0%, the refining cost increases. Therefore, the lower limit of each of O, C, and N may be 0.010% or 0.050%. The lower limit of Si may be 0.001%, the lower limit of the measurement accuracy of chemical analysis.

Ni: 0 to 0.15%, Cr: 0 to 0.25%, Mn: 0 to 0.25%

[0052] Ni, Cr, and Mn are not necessarily contained, and the lower limit of the content is 0. These elements may be contained because they function similarly to Fe. When the contents of Ni, Cr, and Mn increase, intermetallic compounds (Ti₂Ni, TiCr₂, TiMn) which are equilibrium phases are generated, and the fatigue strength and room-temperature ductility deteriorate. Therefore, the contents are preferably Ni: 0 to 0.15%, Cr: 0 to 0.25%, and Mn: 0 to 0.25%. The lower limit of Ni, Cr, and Mn may be 0.001%, 0.001%, or 0.001%, respectively, which are the lower limit of the measurement accuracy of chemical analysis.

[0053] The total amount of Ni, Cr, Mn, and Fe is preferably 0.50% or more and 2.90% or less in consideration of the balance between room temperature tensile strength and room temperature ductility.

Remainder: Ti, and impurities in a total amount of 0.4% or less

[0054] The remainder is Ti and impurities when the chemical composition is (1). Examples of impurity elements include Cl, Na, and Mg mixed in the refining step of titanium, and impurities such as Zr, Sn, Cu, Mo, Nb, and Ta mixed from scrap. As the amount of any impurity increases, a compound with Ti is formed, and the toughness decreases. As a result, workability decreases. In addition, when the total amount of impurities is excessive, ductility is deteriorated, and thus workability is deteriorated. Therefore, the total of impurity elements is preferably controlled to 0.4% or less so as not to impair the effect of the $\alpha+\beta$ titanium alloy shape according to the present embodiment. Also, the amount of each impurity element is preferably 0.1 % or less.

[0055] (2) Al: 4.4 to 5.5%, Fe: 1.4 to 2.3%, Mo: 1.5 to 5.5, O: 0 to 0.20%, C: 0 to 0.080%, N: 0 to 0.05%, Si: 0 to 0.10%, Ni: 0 to 0.15%, Cr: 0 to 0.25%, Mn: 0 to 0.25%, remainder: Ti, and impurities in a total amount of 0.4% or less, and the contents of Fe, Ni, Cr, and Mn, %Fe, %Ni, %Cr, and %Mn, expressed in mass%, satisfy $1.4\% \leq \%Fe + \%Ni + \%Cr + \%Mn \leq 2.3\%$.

Al: 4.4 to 5.5%

[0056] Al is an α -stabilizing element and is an element contained in order to increase the fraction of the α phase. In consideration of the balance among 0.2% proof stress, ductility, and toughness, the amount of Al is preferably 4.4 to 5.5%.

Fe: 1.4 to 2.3%

[0057] Fe is a β -stabilizing element, and has an action of lowering the β transus temperature by being contained in the titanium alloy. In addition, Fe has an action of improving 0.2% proof stress. The amount of Fe is preferably 1.4 to 2.3% in consideration of the balance between 0.2% proof stress and segregation during solidification and elongation.

Mo: 1.5 to 5.5%

[0058] Mo is a β -stabilizing element, and can lower the β transus temperature of the titanium alloy similarly to Fe. In addition, Mo improves 0.2% proof stress, ductility, and fatigue strength, and also improves hot workability. In consideration of the balance with solidifying segregation, the amount of Mo is preferably 1.5 to 5.5%.

O: 0 to 0.20%, C: 0 to 0.080%, N: 0 to 0.050%, Si: 0 to 0.10%

[0059] O, C, N, and Si are not necessarily contained, and the lower limit of the content is 0. These elements are also elements having the same effect as the α -stabilizing element, and have an action of increasing the fraction of the α phase and improving 0.2% proof stress by being contained in the titanium alloy. In consideration of the balance with ductility, the contents are preferably O: 0 to 0.20%, C: 0 to 0.080%, N: 0 to 0.050%, and Si: 0 to 0.10%. However, when the contents of O, C, and N are 0%, the refining cost increases. Therefore, the lower limit of each of O, C, and N may be 0.010% or 0.050%. The lower limit of Si may be 0.001%, the lower limit of the measurement accuracy of chemical analysis.

Ni: 0 to 0.15%, Cr: 0 to 0.25%, Mn: 0 to 0.25%

[0060] Ni, Cr, and Mn are not necessarily contained, and the lower limit of the content is 0. These elements may be contained because they function similarly to Fe. When the contents of Ni, Cr, and Mn increase, intermetallic compounds (Ti_2Ni , TiCr_2 , TiMn) which are equilibrium phases are generated, and the fatigue strength and room-temperature ductility deteriorate. Therefore, the contents are preferably Ni: 0 to 0.15%, Cr: 0 to 0.25%, and Mn: 0 to 0.25%. The lower limit of Ni, Cr, and Mn may be 0.001%, 0.001%, or 0.001%, respectively, which are the lower limit of the measurement accuracy of chemical analysis.

[0061] The total amount of Ni, Cr, Mn, and Fe is preferably 1.40% or more and 2.30% or less in consideration of the balance between room temperature tensile strength and room temperature ductility.

Remainder: Ti, and impurities in a total amount of 0.4% or less

[0062] The remainder is Ti and impurities even when the chemical composition is (2). Examples of impurity elements include Cl, Na, and Mg mixed in the refining step of titanium, and impurities such as Zr, Sn, Cu, Nb, and Ta mixed from scrap. As the amount of any impurity increases, a compound with Ti is formed, and the toughness decreases. As a result, workability decreases. In addition, when the total amount of impurities is excessive, ductility is deteriorated, and thus workability is deteriorated. Therefore, the total of impurity elements is preferably controlled to 0.4% or less so as not to impair the effect of the $\alpha+\beta$ titanium alloy shape according to the present embodiment. Also, the amount of each impurity element is preferably 0.1% or less.

[0063] The cross-sectional form of the $\alpha+\beta$ titanium alloy shape according to the present embodiment is not particularly limited as long as it is a form capable of measuring a twist angle from one end to the other end of the shape. Since the twist angle cannot be measured in the round bar, the circular form is naturally removed from the cross-sectional form, but any other cross-sectional form may be applied to the $\alpha+\beta$ titanium alloy shape according to the present embodiment. Examples of the cross-sectional form include an L shape, a T shape, an H shape, a U shape, a π shape, a + (plus sign) shape, a - (minus sign) shape, and the like. In addition, it may have a form as shown in FIGS. 9A to 9C.

[0064] FIG. 9A is a cross-sectional view of a shape with a form similar to a so-called H-shaped shape. The H-shaped shape has a form in which first and second flat sheets extending in parallel, and a third flat sheet whose end surfaces abut against the surfaces of the first and second flat sheets are integrated. On the other hand, the shape in FIG. 9A has a form in which first, second, and third flat sheets extending in parallel, a third flat sheet whose end surfaces abut against the surfaces of the first and second flat sheets, and a fourth flat sheet whose end surfaces abut against the surfaces of the second and third flat sheets are integrated. That is, the shape in FIG. 9A has a form in which two H-shaped shapes are arranged side by side. A form in which three or more H-shaped shapes are arranged is also allowed.

[0065] FIG. 9B is a cross-sectional view of a shape with a form similar to a so-called T-formed shape. The T-formed shape has a form in which a first flat sheet and a second flat sheet with an end surface abutting against one surface of the flat sheet are integrated. On the other hand, the shape in FIG. 9B has a form in which the first and second flat sheets and a third flat sheet whose end surface abuts against one surface of the second flat sheet are integrated.

[0066] FIG. 9C is also a cross-sectional view of a shape with a form similar to a so-called T-formed shape. The shape in FIG. 9C has a form in which the first and second flat sheets, a third flat sheet whose end surface abuts against one surface of the second flat sheet, and a fourth flat sheet whose end surface abuts against the other surface of the second flat sheet are integrated.

[0067] The form described above is merely an example of the cross-sectional form of the $\alpha+\beta$ titanium alloy shape according to the present embodiment. For example, various variations such as a cross-sectional form in which a hump-shaped projection portion is included in a part of the cross-sectional form exemplified above can be adopted as the cross-sectional form of the $\alpha+\beta$ titanium alloy shape according to the present embodiment.

[0068] Next, a method for manufacturing an $\alpha+\beta$ titanium alloy shape with an excellent form as described above will be described. Hereinafter, the temperature of the shape means the temperature of the surface of the shape measured by a radiation thermometer.

[0069] First, an $\alpha+\beta$ titanium alloy is hot worked by a manufacturing method such as extrusion, die forging, or rolling to obtain a shape with a desired form. The method for manufacturing the shape is not particularly limited, but is preferably hot extrusion in consideration of manufacturing efficiency and the like.

[0070] However, warpage and twist inevitably occur in the shape. According to the normal straightening working, it is difficult to straighten warpage and twist while ensuring the mechanical properties of the shape. In particular, when the method for manufacturing the shape is hot extrusion, the magnitudes of warpage and twist become remarkable. In the method for manufacturing an $\alpha+\beta$ titanium alloy shape according to the present embodiment, this problem is solved by straightening working described later.

[0071] Subsequently, the shape is heated and held in an $\alpha+\beta$ two-phase region. Then, a strain of 0.1 % or more and 8% or less is applied to the shape at least in the longitudinal direction at a straightening temperature of equal to or higher than β transus temperature - 400°C and equal to or lower than β transus temperature - 200°C. Furthermore, a torque that causes a twist in the longitudinal direction to be within $\pm 3.0^\circ$ is further applied to the shape. Thus, the form of the shape is straightened. Here, the β transus temperature is a temperature at which a β single phase is formed during heating. When the straightening temperature is too high, warpage after cooling increases. On the other hand, when the straightening temperature is too low, a large strain is required for straightening the twist, the area fraction of voids increases, and tensile properties and fatigue properties may be deteriorated.

[0072] Generally, twist and warpage behave differently with respect to the straightening temperature, indicating a trade-off relationship. Specifically, warpage is more likely to occur as the straightening temperature is higher, and twist is more likely to remain as the straightening temperature is lower. The warpage occurs when a temperature difference in the shape generated during straightening at a high temperature causes a difference in thermal shrinkage during cooling of the shape. The higher the straightening temperature, the larger the temperature difference in the shape and thus the larger the warpage. On the other hand, twist occurs due to strain introduced during extrusion. The lower the straightening temperature, the larger the elastic limit of the shape. Therefore, even with the same straightening amount, the lower the straightening temperature, the smaller the strain (plastic strain) introduced into the shape. For the above reasons, when the straightening temperature is decreased to eliminate the warpage, the amount of twist is increased because the twist is hardly straightened, and when the straightening temperature is increased to eliminate the twist, the warpage amount is usually increased.

[0073] In order to obtain an excellent form in the $\alpha+\beta$ titanium alloy shape, it is necessary to simultaneously achieve elimination of twist and elimination of warpage. For this purpose, the shape is heated and held in the $\alpha+\beta$ two-phase region from equal to or lower than β transus temperature - 200°C to equal to or higher than β transus temperature - 400°C, and then a strain of 0.1% or more and 8% or less is applied to the shape at least in the longitudinal direction, and a torque that causes a twist in the longitudinal direction to be within $\pm 3.0^\circ$ is also applied to straighten the form. As a result, it is preferable to prevent generation of voids and to achieve both elimination of twist and elimination of warpage. This is also to avoid that the straightening device requires very high rigidity and is very expensive. In the straightening step, it is preferable to apply both the longitudinal strain and the twist in the longitudinal direction to the shape. However, when the shape has a cross-sectional form in which twist hardly occurs, application of twist may be omitted in the straightening step.

[0074] Next, the $\alpha+\beta$ titanium alloy shape after the form straightening is cooled to 500°C or less while applying a predetermined stress. The stress is desirably compressed from the viewpoint of suppressing the formation of voids. However, when the occurrence of buckling and the actual situation of the straightening device are assumed, it is considered that it is industrially much easier to apply the tensile stress. Therefore, it is preferable to apply a tensile stress of 20% or less of 0.2% proof stress at room temperature to the shape. Since the shape shrinks as the temperature decreases, it is difficult to make the tensile stress applied to the shape during cooling constant, but as long as the tensile stress is 20% or less of 0.2% proof stress, the fluctuation of the tensile stress does not cause a problem.

[0075] Further, it is preferable to cool the shape to 500°C or lower while applying a predetermined torque to the shape in addition to the tensile stress. The torque is preferably a value that maintains the twist in the longitudinal direction within $\pm 3.0^\circ$. When these are satisfied, the change (deterioration) in form due to cooling and the residual stress can be reduced. The shape is cooled preferably to 450°C, and further preferably 400°C.

[0076] The method for cooling the shape to 500°C or lower is not particularly limited as long as the titanium alloy can be uniformly cooled. The cooling means may be natural cooling or accelerated cooling. Specifically, examples of the accelerated cooling include cooling in a gas atmosphere such as Ar, N, H, or He, cooling in a liquid such as water or oil, and the like.

[0077] In order to uniformly cool the titanium alloy, the average cooling rate from the straightening temperature to 500°C is preferably 10°C/s or less, 1°C/s or less, 0.5°C/s or less, or 0.1°C/s or less. In addition, when the stress to be applied is the tensile stress as described above, it is considered that the compressive stress further remains on the surface of the shape in which the temperature decreases faster than the inside. The residual stress greatly affects working into parts and products, but from the viewpoint of improving fatigue properties, the compressive residual stress is generally desirable. That is, it is desirable to adjust the residual stress to some extent. The "average cooling rate from the straightening temperature to 500°C" is a value obtained by dividing the difference between the straightening temperature and 500°C by the time required for the shape temperature to decrease from the straightening temperature to 500°C.

[0078] After straightening, by cooling while applying stress or/and torque, stress concentrates on a portion with poor form, for example, a portion with large warpage, a portion with large twist, or the like. Then, local plastic deformation occurs in a portion where a large stress acts. This effectively and efficiently improves the form, relaxes the residual stress, maintains an excellent form due to hot straightening at high temperature, significantly suppresses deterioration of the form such as warpage or twist occurring during cooling, and further can reduce the residual stress in the titanium alloy. Since the residual stress is effectively and efficiently reduced in the shape cooled while applying stress or/and torque in this manner, the form change in the case of cutting after cooling is also reduced.

[0079] The value of the torque applied during cooling can be appropriately set according to the cross-sectional form of the shape. For example, as described above, a torque that maintains the twist in the longitudinal direction within $\pm 3.0^\circ$ is preferable. A torque that maintains the twist in the longitudinal direction within $\pm 2.0^\circ$ is more preferable, and one within $\pm 1.0^\circ$ is further preferable. The torque during cooling may be constant, but may vary within a predetermined region. For example, the torque can be increased as the temperature decreases.

[0080] As described above, the stress applied during cooling is preferably a tensile stress of 20% or less of 0.2% proof stress of the shape at room temperature. The stress applied during cooling is more preferably 15% or less and further preferably 10% or less of 0.2% proof stress of the shape at room temperature. The lower limit of the tensile stress is not specified, but is preferably 1 % or more of 0.2% proof stress of the shape at room temperature from the viewpoint of remaining of the form and compressive stress. When these are satisfied, the change (deterioration) in form due to plastic deformation or cooling and the residual stress can be reduced. The tensile stress during cooling may be constant, but may vary within a predetermined region. For example, a tensile stress corresponding to the elastic limit at each temperature can be applied.

[0081] There is no particular limitation on the atmosphere during the treatment from the start of the straightening of the form of the shape to cooling the shape to 500°C or lower, and the treatment may be performed in the atmosphere, for example. On the other hand, if necessary, even if the surroundings of a part or the whole of the shape are set to different atmospheres in a predetermined temperature region or in all temperature regions, the atmospheres are allowed as long as the atmospheres do not significantly deteriorate surface properties. As an example, in the present manufacturing method, it is possible to apply a gas such as argon or nitrogen to the atmosphere in the step of straightening the shape. Specifically, for example, oxidation is prevented by covering the entire device with a chamber, or oxidation is prevented by spraying a sealing gas to a part of the device.

[0082] After the form of the shape is straightened, the shape temperature may be held at the temperature at which the straightening is performed. In addition, the shape temperature may be held in a predetermined temperature region of equal to or higher than β transus temperature - 400°C and equal to or lower than β transus temperature - 200°C. Furthermore, it is also possible to hold the shape in a predetermined temperature region, for example, 500 to 650°C, during the cooling of the shape. Such temperature holding is performed to remove strain generated during straightening and thermal strain generated during cooling, and further enhances the characteristics of the shape according to the present embodiment.

[0083] There are standards for 0.2% proof stress and elongation in the standards for Ti-6Al-4V round bar which is a general-purpose $\alpha+\beta$ titanium alloy, that is, JIS H4650 and ASTM B348. Specifically, the standard specifies that 0.2% proof stress is preferably 828 MPa or more and elongation is preferably 10% or more. However, these standards do not define the microstructure. Therefore, even if the microstructure of the shape is an acicular microstructure, the same lower limit as that of the equiaxed microstructure with excellent strength-ductility balance is provided.

[0084] According to the method for manufacturing an $\alpha+\beta$ titanium alloy shape according to the present embodiment, when the straightening amount is 8% or less, the 0.2% proof stress is improved without lowering the elongation, a strength-ductility balance satisfying ASTM B348 is obtained, and the fatigue strength is not lowered. This is considered to be because dislocations gather at the grain boundaries when stress is applied to the titanium alloy to straighten the titanium alloy, and the grain boundaries are strengthened without forming voids.

[0085] The standard AMS2245B has standards for twist and warpage. Specifically, it is preferably specified as follows: a twist of 1° or less in 1 foot and within $\pm 3.0^\circ$ in total length, and a warpage within ± 0.65 mm per 300 mm (warpage height

(mm)/total length (m) = ± 2.17).

[0086] However, in a more complicated and highly accurate form, it is necessary to achieve more severe specified values of warpage and twist. It is preferably set as follows: a twist of 0.5° or less in 1 foot and within $\pm 2.0^\circ$ in total length, and a warpage within ± 0.45 mm per 300 mm (warpage height (mm)/total length (m) = ± 1.50). The titanium alloy shape according to the present embodiment can achieve these values.

[0087] The size of the $\alpha+\beta$ titanium alloy shape according to the present embodiment is not particularly limited. According to a manufacturing facility usually used at the present time, the shape usually has a thickness of 30 to 300 mm and a total length of 5 to 20 m. Here, the thickness of the shape is the diameter of the smallest circle that can include the cross section of the shape. For example, when the cross section of the shape is a triangle, the thickness of the shape is a diameter of a circle passing through all three vertices of the cross section of the shape, that is, a circumscribed circle of the cross section of the shape. However, in principle, even a larger shape can be manufactured by using a manufacturing facility corresponding thereto. On the other hand, a shape with a total length of less than 5 m may be manufactured by hot extrusion. In addition, after a shape with a length of 5 m or more is manufactured, the shape may be cut to manufacture an $\alpha+\beta$ titanium alloy shape with a total length of less than 5 m. In either case, the performance of the titanium alloy shape according to the present embodiment is maintained.

[Examples]

[0088] Hereinafter, the effect of improving warpage and twist after hot straightening according to the present invention will be described using Examples. Note that the present invention is not limited to the following Examples.

(Examples)

[0089] In order to confirm the influence of the straightening amount on tensile properties and fatigue properties of a shape, T-formed or U-formed test materials (FIG. 3) in which a temperature difference is likely to occur in the cross section were manufactured using titanium alloys with the components and β transus temperature during heating shown in Table 1. The components shown in Table 1 are values measured after hot straightening described later. However, hot extrusion and hot straightening do not affect the component change of the titanium alloy.

[0090] The titanium alloy with the components in Table 1 has a two-phase microstructure composed of α phase and β phase between room temperature and the β transus temperature. As a test material, an actual ingot was subjected to final hot forging in an $\alpha+\beta$ temperature region, and the obtained ϕ 200 billet was heated to a β single-phase temperature region and extruded to obtain an $\alpha+\beta$ titanium alloy shape.

[0091] The β transus temperature of the titanium alloy was obtained by the following procedure.

[0092] First, estimated value $T\beta$ of the β transus temperature of the titanium alloy was calculated by substituting the amount of the element corresponding to each symbol into the element symbol described in the following formula.

$$T\beta = 882 + 21.1 \times [\text{Al}] - 13.9 \times [\text{V}] - 13.9 \times [\text{Fe}] - 9.5 \times [\text{Mo}] - 12.1 \times [\text{Cr}] + 23.3 \times [\text{Si}] + 183.3 \times [\text{O}] + 580 \times [\text{C}] + 1040 \times [\text{N}]$$

[0093] However, the above-described estimated value is not accurate, and may be different from the actual β transus temperature by about 100°C . Therefore, the true β transus temperature was obtained by the following procedure.

(A) The titanium alloy is heated to various temperatures within a temperature region of β transus temperature $\pm$ about 50°C , followed by rapid cooling. The heating temperature is changed by 5°C within the above region.

(B) Various microstructures obtained in the above (A) are observed to confirm whether or not an acicular microstructure is formed in these microstructures. The heating temperature of the titanium alloy in which the acicular microstructure was confirmed exceeded the β transus temperature.

(C) The smallest value among the heating temperatures at which the acicular microstructure is obtained is regarded as the β transus temperature of the titanium alloy.

[0094] If an acicular microstructure is obtained at all the heating temperatures, the above (A) to (C) are repeated in a temperature region lower than the above temperature region. When the acicular microstructure is not obtained at all the heating temperatures, the above (A) to (C) are repeated in a temperature region higher than the above temperature region.

[Table 1]

Alloy No.	Alloy component (mass%)										β Transus (°C)
	Al	Fe	Mo	O	C	N	Si	Ni	Cr	Mn	
1	5.2	1.2	-	0.19	0.011	0.002	-	-	-	-	1010
2	5.4	1.0	-	0.24	0.003	0.003	-	0.13	-	-	1020
3	5.0	0.7	-	0.16	0.061	0.015	-	-	0.23	-	1025
4	6.3	1.9	-	0.09	0.002	0.002	-	-	-	0.23	995
5	5.4	2.1	-	0.14	0.012	0.002	0.48	-	-	-	975
6	5.4	2.4	-	0.14	0.010	0.045	-	-	-	-	1020
7	4.6	2.3	5.0	0.09	0.002	0.002	0.05	-	-	-	935
8	5.2	1.8	1.7	0.16	0.021	0.003	0.04	0.13	-	-	952
9	5.0	1.5	3.0	0.16	0.005	0.015	0.03	-	0.23	-	957
10	5.0	1.5	3.0	0.17	0.007	0.002	0.08	-	-	0.23	955
11	5.2	1.7	2.9	0.14	0.002	0.002	0.04	-	-	-	955
In the table, "-" indicates that the element was not actively added.											

[0095] The obtained shape was hot straightened under various straightening conditions. Subsequently, the shape was allowed to cool to a predetermined temperature in the atmosphere. Table 2 shows the straightening temperature (see the column of "Straightening temperature"), the amount of strain in the longitudinal direction applied to the shape at the straightening temperature (see the column of "Longitudinal strain"), the twist in the longitudinal direction applied to the shape at the straightening temperature (see the column of "Twist angle before cooling"), and the cooling stop temperature (see the column of "Removal temperature"). Further, the tensile stress applied to the shape during cooling of the shape (see the column of "Tensile stress during cooling"), the holding temperature of the shape during cooling (see the column of "Holding temperature during cooling"), and the average cooling rate of the shape from the straightening temperature to 500°C (see the column of "Cooling rate") are also shown in Table 2.

[0096] For example, in No. 1, a tensile stress of 75 MPa and a torque for generating a twist of -0.6° were applied to the test material at a straightening temperature of 720°C. Then, the test material was allowed to cool to 400°C while the tensile stress and the torque were applied, and the test material was removed from the tension applying device. The average cooling rate of the shape from the straightening temperature to 500°C was set to 0.5°C/s.

[0097] On the other hand, in No. 17, no torque was applied before cooling. Therefore, in No. 17, it is described as "Absent" in the column of "Presence or absence of torque during cooling". Also, in No. 17, "-" was written in the column of "Twist angle during cooling" as a symbol indicating that no torque was applied.

[0098] In Example 18, the cooling at the time of the straightening working is interrupted at 600°C, and the temperature is held here. In Example 18, the average cooling rate when the surface temperature of the shape falls from 720°C to 600°C is set to 0.5°C/sec, the surface temperature of the shape is held at 600°C for 10 minutes, and the average cooling rate when the surface temperature of the shape falls from 600°C to 500°C is set to 0.5°C/s.

<Fatigue Test>

[0099] In the measurement of fatigue strength, a round bar test piece with a diameter of 5.08 mm and a length of parallel portion of 15.24 mm was prepared from circled portions in FIG. 3 so as not to include a region with a depth of less than 0.5 mm from the surface of the shape. Using the round bar test piece, a fatigue test was performed under the conditions of a stress ratio $R = \sigma_{\min} / \sigma_{\max} = 0.1$ (both $\sigma_{\min}$ and $\sigma_{\max}$ are tensile stress) and room temperature, and the absolute maximum value of strength $\sigma_{\max}$ at which the round bar test piece did not fracture at the number of repetitions of 1.0×10^7 times was defined as the fatigue strength.

[0100] Furthermore, for each shape, 0.2% proof stress, elongation, void area fraction, absolute maximum value of residual stress, absolute maximum value of dimensional variation after cutting, twist after straightening, and warpage after straightening were measured. The results are shown in Table 2.

[0101] The 0.2% proof stress and elongation were evaluated in accordance with ASTM E8 by collecting test pieces with a length of parallel portion of 28 mm and a diameter of 6.25 mm from the shape and performing a tensile test at a speed of 0.005/min (8.3×10^{-5} /s) at a strain of 2% or less and at a speed of 0.1/min (1.67×10^{-3} /s) at a strain of 2% or more. The

collection positions of the test pieces were circled portions in FIG. 3.

[0102] In addition, regarding the fatigue strength, 0.2% proof stress, and elongation, similar results can be obtained by preparing the test pieces so as not to include a region with a depth of less than 0.5 mm from the surface.

[0103] The void area fraction and the absolute maximum value of residual stress were evaluated by the above-described method.

[0104] As shown in FIGS. 6A and 6B, the absolute maximum value of dimensional variation after cutting was evaluated by measuring the dimensional variation due to a part of the cross section inclined with cutting with a caliper. FIG. 6A is a cross-sectional view of an example indicated as "T" in the column of "Form", and FIG. 6B is a cross-sectional view of an example indicated as "U" in the column of "Form".

[0105] Warpage and twist after straightening were measured according to AMS2245B.

[0106] In Table 2, those underlined are outside the scope of the present invention.

[0107] Furthermore, microstructure evaluation was also performed. The evaluation of the microstructure was performed by the following procedure. First, test pieces for microstructure observation were collected from a cross section with a length of 1/2 from the obtained shape. The dimension of the test piece for microstructure observation is not particularly limited, and the cross section itself of the shape with a small cross-sectional area may be used as the test piece for microstructure observation. Here, 10 mm square test pieces were collected. The collection positions were the circle positions in FIG. 3. The observed section was mirror-polished and further corroded using fluonitric acid to exhibit a microstructure. Then, the microstructure was observed using an optical microscope. As a result of the observation, it was confirmed that the metallographic structure was an acicular microstructure in all Examples.

[0108] It was confirmed that the metallographic structure was an acicular microstructure at the circle positions in FIG. 3 located in a region with a depth of 0.5 mm or more from the surface of the shape. On the other hand, in a region with a depth of less than 0.5 mm from the surface of the shape, that is, in the surface layer region, a site where the acicular microstructure and the equiaxed microstructure are mixed was observed. This is presumed to be because during hot extrusion, the temperature tends to decrease in the surface layer region, and processing strain is introduced in a temperature region equal to or lower than the β transus temperature. In the region with a depth of 0.5 mm or more from the surface of the shape, the metallographic structure is preferably mainly composed of an acicular microstructure, and particularly preferably, the proportion of the acicular microstructure in the metallographic structure is 100%.

[0109] For the corroded test piece, using an optical microscope at a magnification of 200 times, the size of the measurement region was set to 7 mm square, 15 vertical straight lines and 15 horizontal straight lines were drawn at equal intervals in the measurement region, and the prior β grain size was measured by a cutting method.

[0110] In all Examples, the average prior β grain size was 500 μm or less. In some of Examples, the average prior β grain size was 60 μm .

[Table 2]

No.	Classification	Alloy No.	Form	Straightening temperature /°C	Longitudinal strain (%)	Twist angle before cooling/°	Presence or absence of torque during cooling	Tensile stress during cooling /MPa	Cooling rate /°C·s ⁻¹	Holding temperature during cooling /°C	Removal temperature /°C
1	Example	1	T	720	3.0	-0.6	Present	75	0.5	Not held	400
2		2	T	720	3.0	-0.5	Present	75	0.5	Not held	400
3		3	T	720	3.0	0.4	Present	75	0.5	Not held	400
4		4	T	720	3.0	0.6	Present	75	0.5	Not held	400
5		5	T	720	3.0	0.5	Present	75	0.5	Not held	400
6		6	T	720	3.0	0.6	Present	75	0.5	Not held	400
7		7	T	720	3.0	0.7	Present	75	0.5	Not held	400
8		8	T	720	3.0	-0.6	Present	75	0.5	Not held	400
9		9	T	720	3.0	-0.7	Present	75	0.5	Not held	400
10		10	T	720	3.0	0.5	Present	75	0.5	Not held	400
11		11	T	720	3.0	0.2	Present	75	0.5	Not held	400
12		1	T	800	3.0	0.5	Present	75	0.5	Not held	400
13		1	T	720	8.0	1.1	Present	75	0.5	Not held	400
14	Comparative Example	1	T	720	3.0	-0.4	Present	<u>0</u>	0.5	Not held	400
15		1	T	<u>600</u>	3.0	-0.7	Present	<u>0</u>	0.5	Not held	400
16		1	T	720	3.0	-0.5	Present	75	0.5	Not held	<u>550</u>
17		1	T	720	3.0	-	<u>Absent</u>	75	0.5	Not held	400
18	Example	1	T	720	3.0	1.0	Present	75	0.5	600°C	400
19		1	T	720	3.0	0.9	Present	75	0.1	Not held	400
20		1	U	720	3.0	0.2	Present	75	0.5	Not held	400
21	Comparative Example	1	T	720	<u>8.5</u>	-0.4	Present	75	0.5	Not held	400
22		7	T	720	<u>8.5</u>	0.5	Present	75	0.5	Not held	400
23		11	T	600	<u>0.0</u>	<u>68.5</u>	<u>Absent</u>	<u>0</u>	0.5	Not held	25
24	Example	1	T	720	3.0	0.4	Present	180	0.5	Not held	400
25		1	T	720	3.0	-0.2	Present	75	12.0	Not held	400

*Underlined parts indicate outside the scope of the present invention.

[Table 3]

No.	0.2% Proof stress /MPa	Elongation (%)	Fatigue strength /MPa	Void area fraction $\times 10^6$ (%)	Maximum residual stress /MPa	Absolute maximum value of dimensional change after cutting /mm	Twist after straightening /°	Warpage amount (mm)/total length (m) after straightening
1	840	13.5	520	< 1	340	0.58	-1.2	-0.40
2	850	12.5	525	< 1	350	0.64	-1.4	-0.70
3	882	13.5	560	< 1	330	0.54	1.2	-0.60
4	851	12.4	500	< 1	350	0.67	-1.8	-0.50
5	910	12.5	560	< 1	330	0.81	1.2	-0.80
6	885	12.1	520	< 1	340	0.72	1.5	-0.70
7	1020	10.2	650	< 1	320	0.61	1.2	-0.20
8	1015	10.1	620	< 1	340	0.52	2.4	-0.10
9	1060	10.3	660	< 1	330	0.55	-1.8	-1.00
10	1045	10.4	640	< 1	350	0.68	-0.6	-0.40
11	1040	10.2	620	< 1	380	0.71	-1.9	-1.00
12	830	13.4	540	< 1	380	0.45	-1.3	-1.20
13	855	13.1	510	6.4	370	0.81	-1.4	-0.60
14	838	13.1	500	< 1	450	2.20	1.4	<u>-5.20</u>
15	862	10.2	460	3.4	440	1.41	<u>-3.1</u>	-1.30
16	852	13.0	510	< 1	520	2.25	-1.5	<u>-55.10</u>
17	848	12.9	530	< 1	380	0.72	<u>6.0</u>	-1.20
18	862	12.1	530	< 1	330	0.53	-1.5	-0.40
19	860	12.4	520	< 1	300	0.48	1.4	-0.40
20	842	13.0	500	< 1	330	0.52	0.8	1.40
21	895	12.5	<u>430</u>	<u>19.5</u>	330	0.64	-2.1	-0.14
22	1025	<u>8.1</u>	460	<u>25.3</u>	350	0.55	1.4	-0.09
23	926	10.5	580	< 1	580	4.50	<u>68.5</u>	1.75
24	856	10.2	450	9.8	390	4.20	-2.1	1.10
25	880	12.7	545	< 1	590	4.14	1.8	0.70

[0111] Nos. 1 to 13 and 18 to 20 are examples in which air cooling was performed while applying a torque that maintains an angle during cooling and a tensile stress after straightening at various alloy types and temperatures. In all cases, since the elongation amount during straightening, that is, the longitudinal strain was 8% or less, the test pieces had a 0.2% proof stress of 830 MPa or more, an elongation of 10% or more, and a fatigue strength of 450 MPa or more, and had excellent strength-ductility balance and fatigue properties. Furthermore, since cooling was performed while applying a torque and a tensile stress during cooling after hot straightening, the maximum residual stress exceeded +400 MPa, the absolute maximum value of the dimensional change after cutting was 2.5 mm or less, and a shape excellent in a form with little warpage and twist even as hot straightening can be obtained. In No. 13, since the strain in the longitudinal direction during straightening was 8% that is the upper limit, voids were slightly generated, but good mechanical properties were secured. In No. 24, since a tensile stress exceeding 20% of 0.2% proof stress at room temperature was applied to the shape, a void was slightly generated, but good mechanical properties were secured. In No. 25, since the shape was forcibly cooled using a mist while being retained by the straightener, the cooling rate was high, and as a result, the maximum residual stress in the cross section was increased. However, also in the shape of No. 25, warpage and twist were small, and proof stress, fatigue strength, and ductility were within acceptable regions.

[0112] Nos. 14 to 15 are shapes obtained by cooling the shapes while maintaining the length after straightening to a low

temperature, without applying a tensile stress during cooling after hot straightening, and removing the shapes from the straightener. Therefore, in No. 14 in which the hot straightening temperature was 720°C, the warpage amount (mm)/the total length (m) after straightening was out of the region of ± 2.17 , the maximum residual stress exceeded +400 MPa, and the absolute maximum value of dimensional variation before and after cutting also exceeded 2.0 mm. On the other hand, in

No. 15 in which the hot straightening temperature was 600°C, which is lower than the β transus temperature of -400°C, the twist was not straightened by the elongation amount of 3%, and the twist was out of the region of $\pm 3.0^\circ$ even after cooling.

[0113] In No. 16, since the removal temperature after hot straightening exceeded 500°C, thermal stress was generated during cooling, the maximum residual stress exceeded +400 MPa, and the absolute maximum value of warpage after cooling and dimensional variation before and after cutting exceeded 2.0 mm.

[0114] In No. 17, a torque that maintains twist during cooling was not applied. Therefore, the spring back during cooling was large, and the twist of the shape after cooling was out of the region of $\pm 3.0^\circ$.

[0115] No. 18 was held at 500 to 650°C during cooling, and the cooling rate of No. 19 was 0.1°C/s or less, so that the 0.2% proof stress was higher than that of other alloys with the same alloy component, which exceeded 850 MPa.

[0116] In Nos. 21 to 22, since the strain in the longitudinal direction during straightening exceeded 8%, a large number of voids were observed inside the shape, and ductility or fatigue strength fell below the lower limit depending on the alloy type.

[0117] No. 23 was twisted during cooling without performing the straightening in the two-phase region, and as a result, a large twist occurred after the straightening working.

[0118] According to the present invention, it was confirmed that the form of the $\alpha+\beta$ titanium alloy excellent in strength, elongation, and fatigue properties was significantly improved by form straightening, and stable manufacturing was possible.

[Brief Description of the Reference Symbols]

[0119]

- 1 Container
- 2 Stem
- 3 Dummy block
- 4 Die
- 5 Billet
- 6 Shape
- 11 Extrusion direction

Claims

1. An $\alpha+\beta$ titanium alloy shape comprising an acicular microstructure, wherein

- a 0.2% proof stress is 830 MPa or more,
- an elongation is 10% or more,
- a fatigue strength is 450 MPa or more,
- an area fraction of voids is $1.0 \times 10^{-5}\%$ or less,
- a twist angle from one end to the other end is within $\pm 3.0^\circ$, and
- a warpage height (mm)/total length (m) is within ± 2.17 .

2. The $\alpha+\beta$ titanium alloy shape according to claim 1, wherein the 0.2% proof stress is 850 MPa or more.

3. The $\alpha+\beta$ titanium alloy shape according to claim 1 or 2, wherein the area fraction of voids is $1.0 \times 10^{-6}\%$ or less.

4. The $\alpha+\beta$ titanium alloy shape according to any one of claims 1 to 3, wherein the average prior β grain size is 500 μm or less.

5. The $\alpha+\beta$ titanium alloy shape according to any one of claims 1 to 4, wherein the maximum residual stress in the cross section is +400 MPa or less.

6. The $\alpha+\beta$ titanium alloy shape according to any one of claims 1 to 5, wherein the $\alpha+\beta$ titanium alloy shape is an extruded shape.

7. The $\alpha+\beta$ titanium alloy shape according to any one of claims 1 to 6, comprising in mass%,

Al: 4.4 to 6.5%,
 Fe: 0.5 to 2.9%,
 Si: 0 to 0.50%,
 O: 0 to 0.25%,
 C: 0 to 0.08%,
 N: 0 to 0.05%,
 Ni: 0 to 0.15%,
 Cr: 0 to 0.25%, and
 Mn: 0 to 0.25%,
 with the remainder being Ti and impurities,
 wherein the contents of Fe, Ni, Cr, and Mn, %Fe, %Ni, %Cr, and %Mn, expressed in mass%, satisfy $0.5\% \leq \%Fe + \%Ni + \%Cr + \%Mn \leq 2.9\%$.

8. The $\alpha+\beta$ titanium alloy shape according to any one of claims 1 to 6, comprising in% by mass,

Al: 4.4 to 5.5%,
 Fe: 1.4 to 2.3%,
 Mo: 1.5 to 5.5%,
 O: 0 to 0.20%,
 C: 0 to 0.08%,
 N: 0 to 0.05%,
 Si: 0 to 0.10%,
 Ni: 0 to 0.15%,
 Cr: 0 to 0.25%, and
 Mn: 0 to 0.25%,
 with the remainder being Ti and impurities,
 wherein the contents of Fe, Ni, Cr, and Mn, %Fe, %Ni, %Cr, and %Mn, expressed in mass%, satisfy $1.4\% \leq \%Fe + \%Ni + \%Cr + \%Mn \leq 2.3\%$.

9. A method for manufacturing the $\alpha+\beta$ titanium alloy shape according to any one of claims 1 to 8, the method comprising:

hot working an $\alpha+\beta$ titanium alloy to obtain a shape;
 heating the shape to a straightening temperature of equal to or higher than β transus temperature - 400°C and equal to or lower than β transus temperature - 200°C, applying a strain of 0.1% or more and 8% or less in a longitudinal direction at the straightening temperature, and further applying a torque that makes a twist in the longitudinal direction of the shape within $\pm 3.0\%$; and
 cooling the shape to 500°C or lower while applying tensile stress and the torque to the shape.

10. The method for manufacturing an $\alpha+\beta$ titanium alloy shape according to claim 9, wherein the tensile stress applied during cooling of the shape is 20% or less of 0.2% proof stress at room temperature.

11. The method for manufacturing an $\alpha+\beta$ titanium alloy shape according to claim 9 or 10, further comprising holding the shape at 500 to 650°C during cooling of the shape.

12. The method for manufacturing an $\alpha+\beta$ titanium alloy shape according to any one of claims 9 to 11, wherein an average cooling rate of the shape from the straightening temperature to 500°C is 10°C/s or less.

FIG. 1

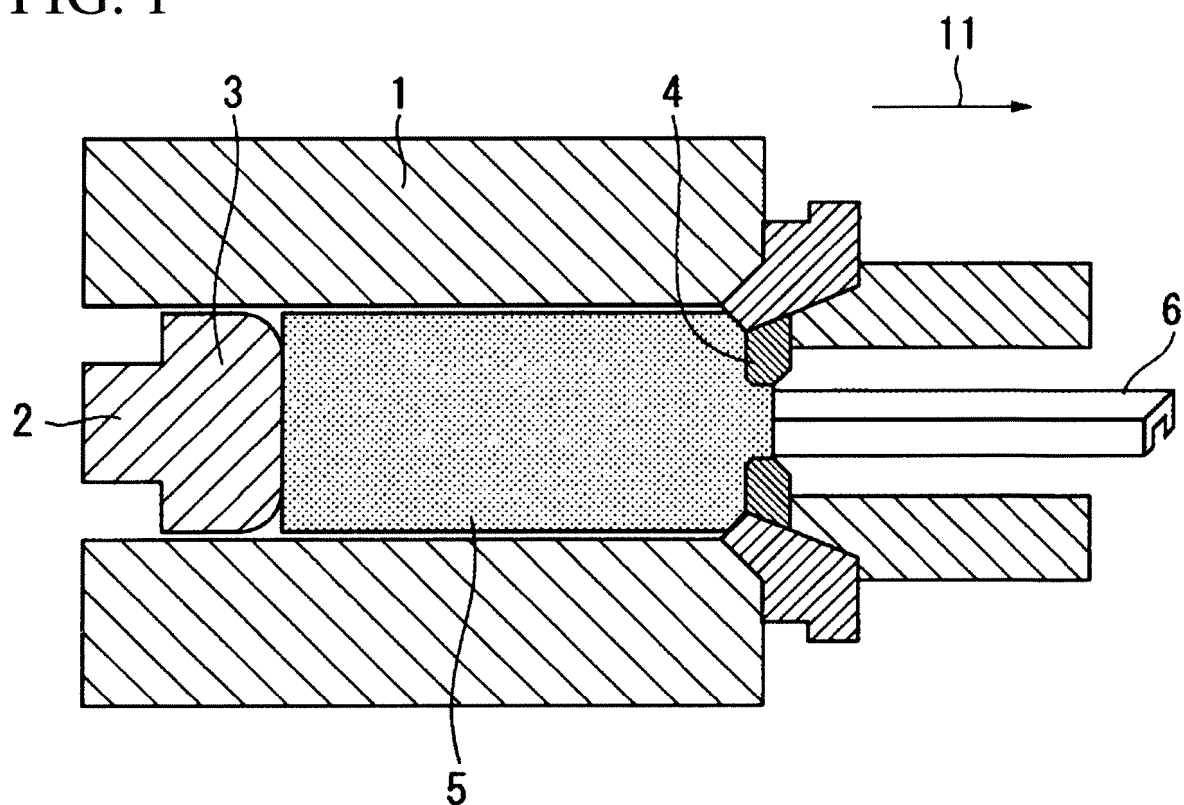


FIG. 2

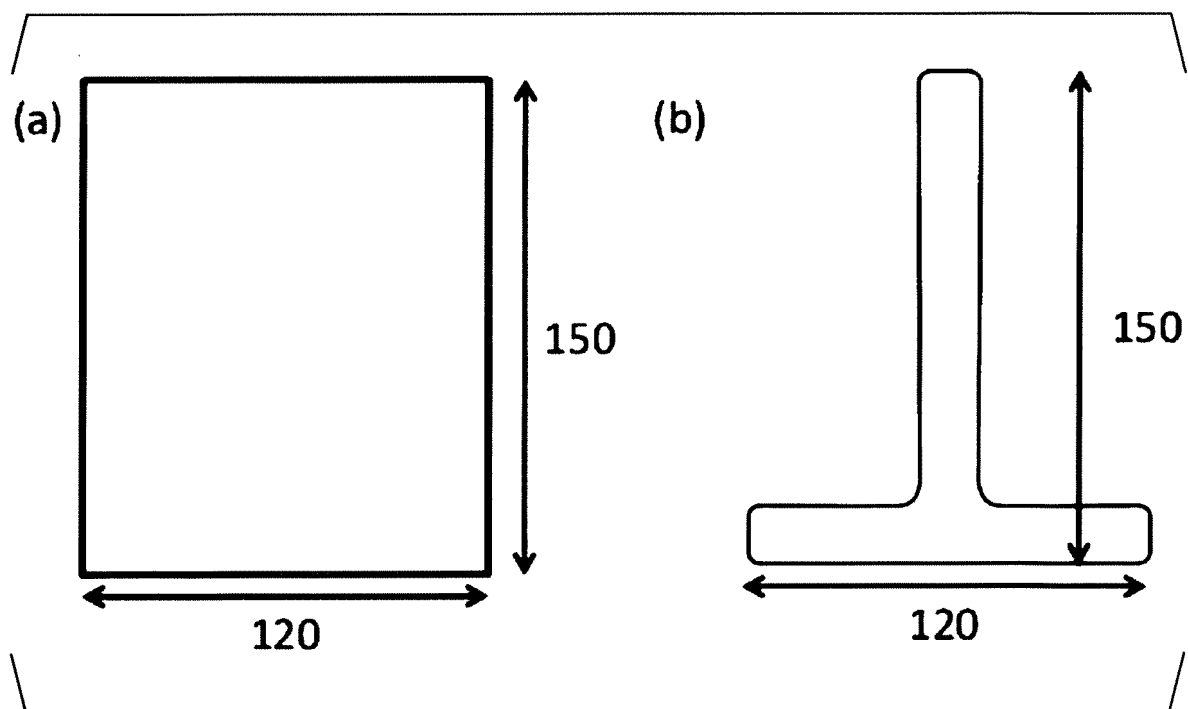


FIG. 3

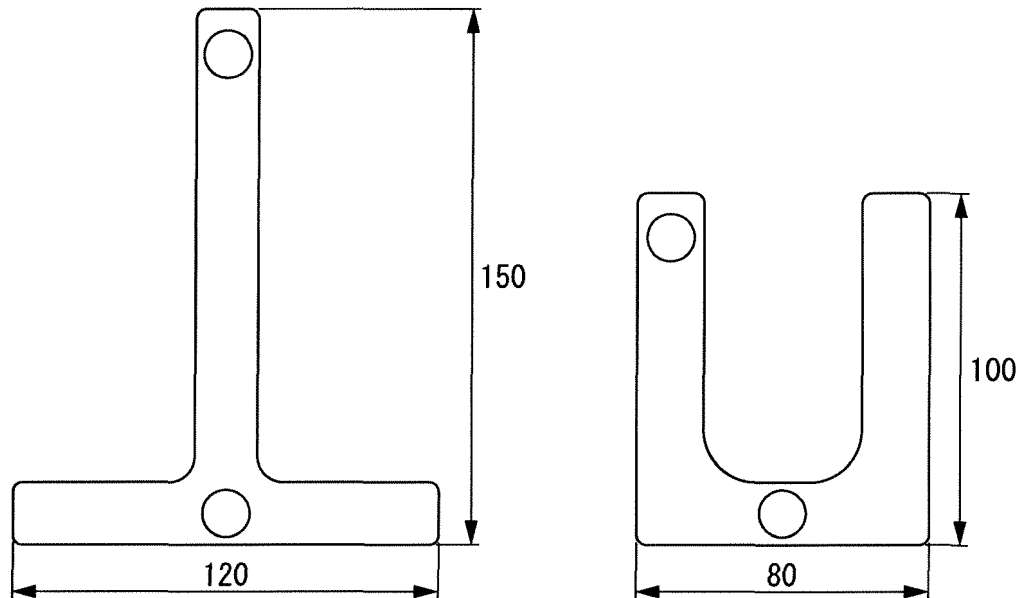


FIG. 4

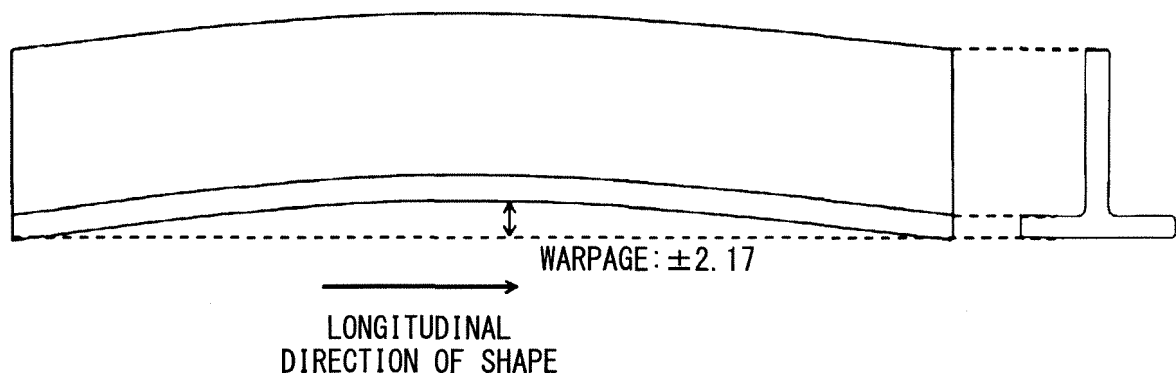


FIG. 5

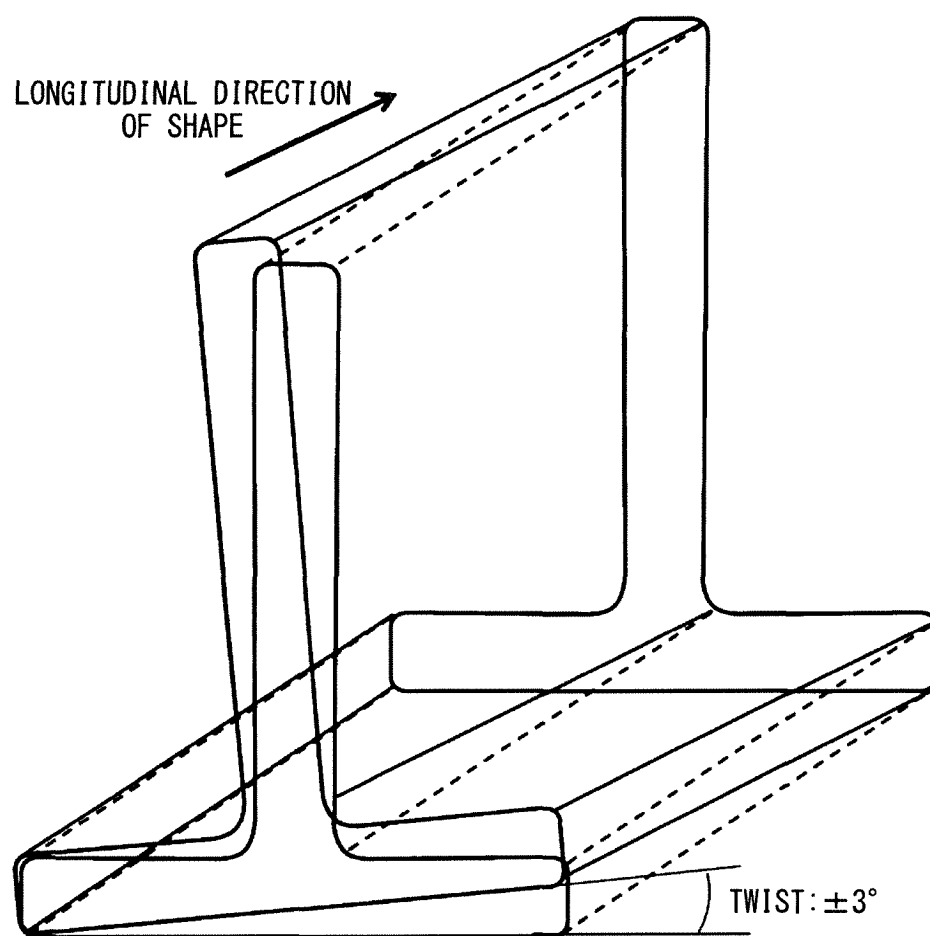


FIG. 6A

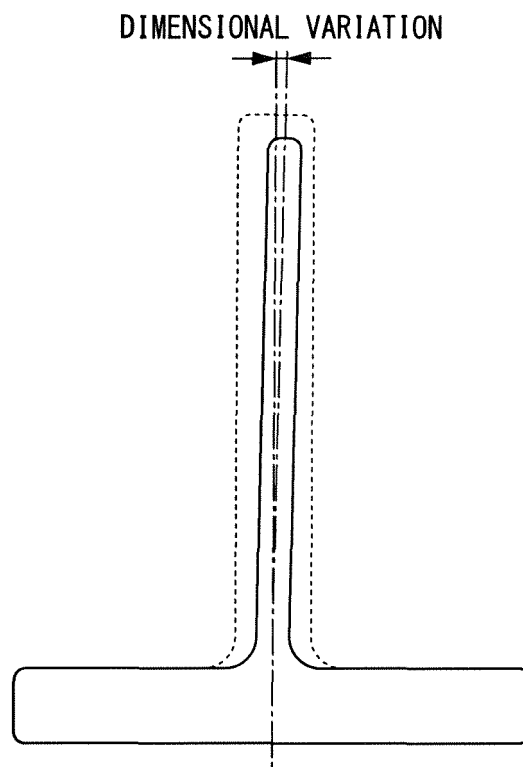


FIG. 6B

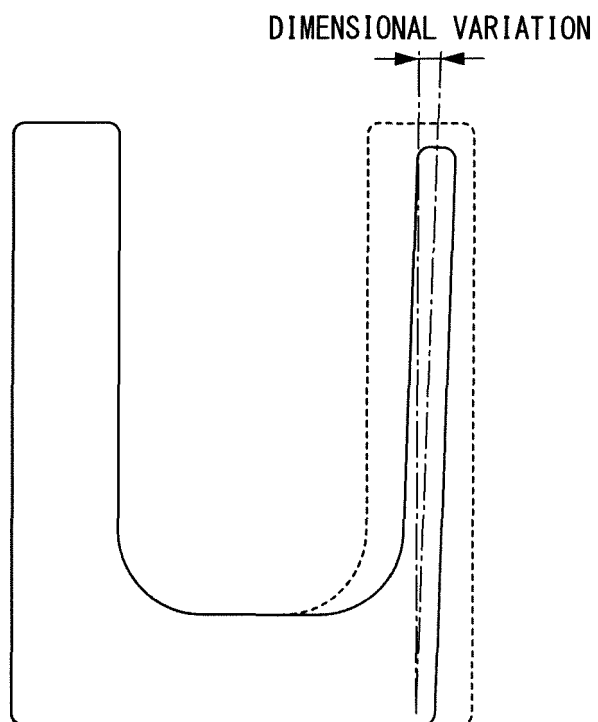


FIG. 7A

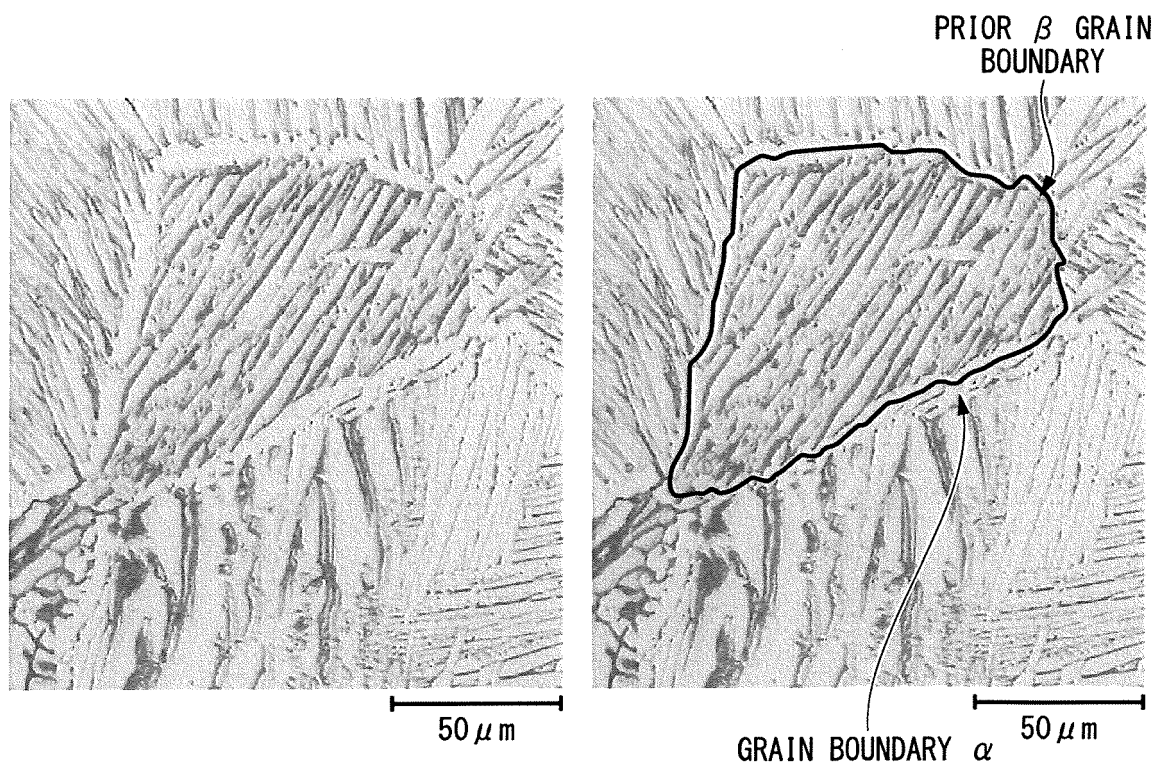


FIG. 7B

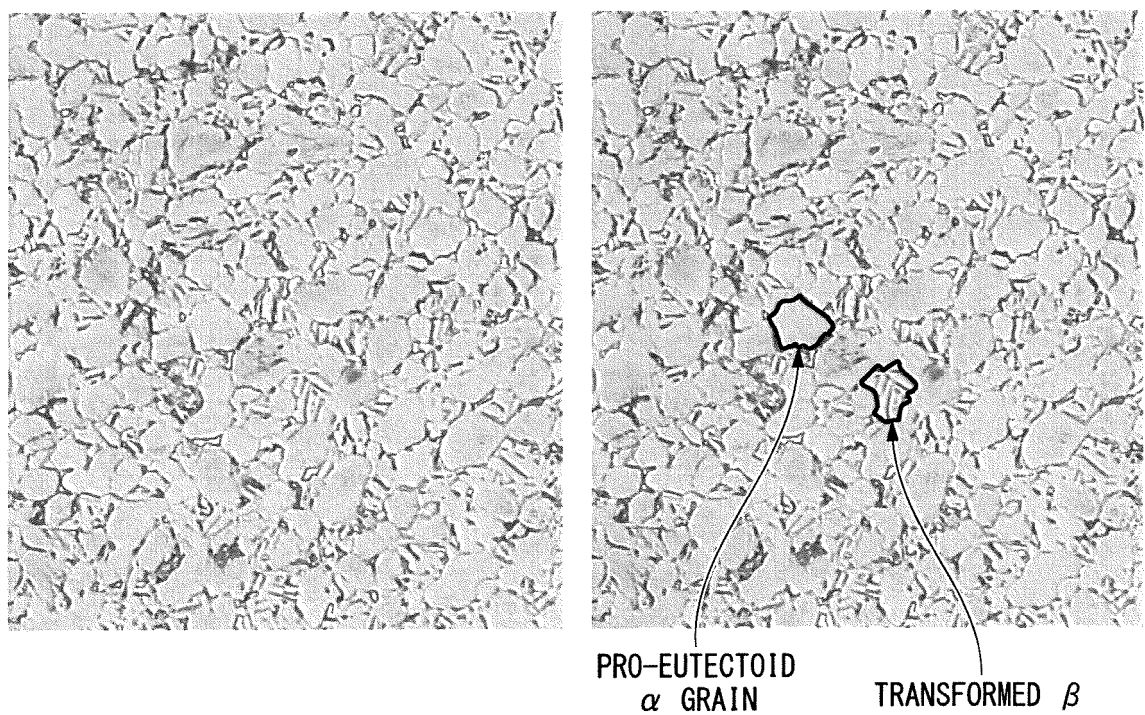


FIG. 8

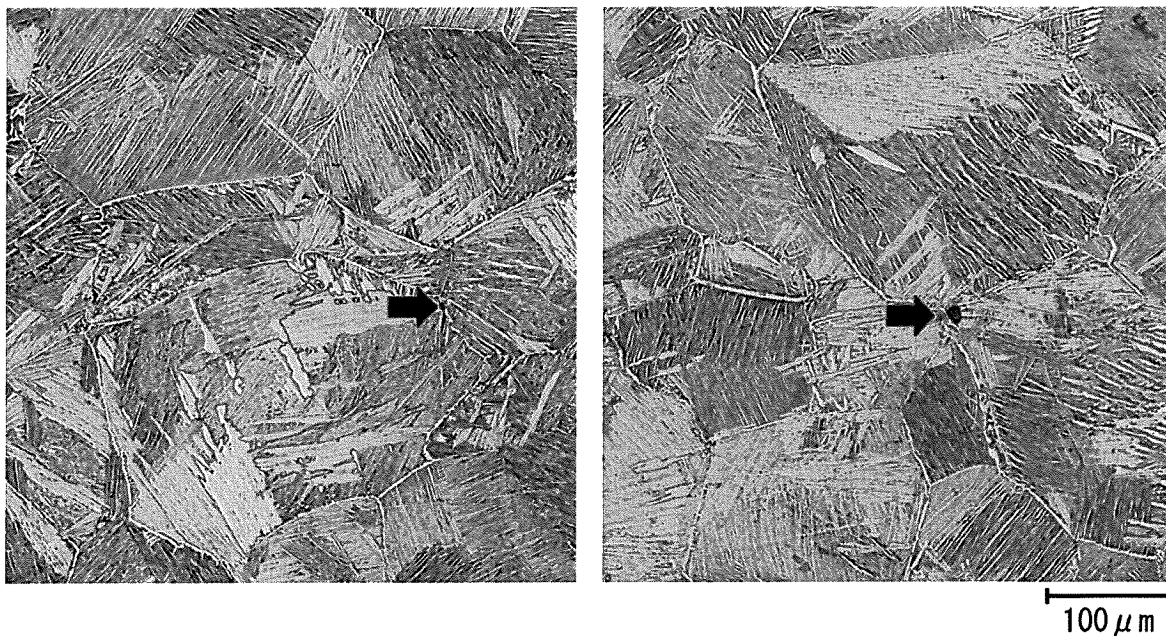


FIG. 9A

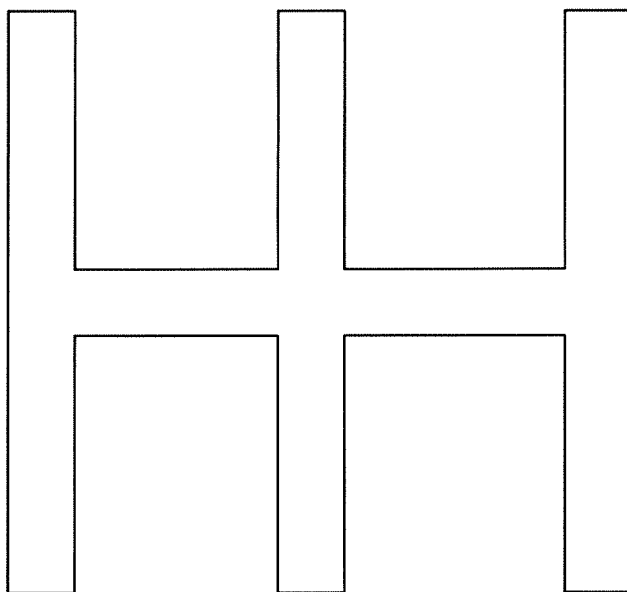


FIG. 9B

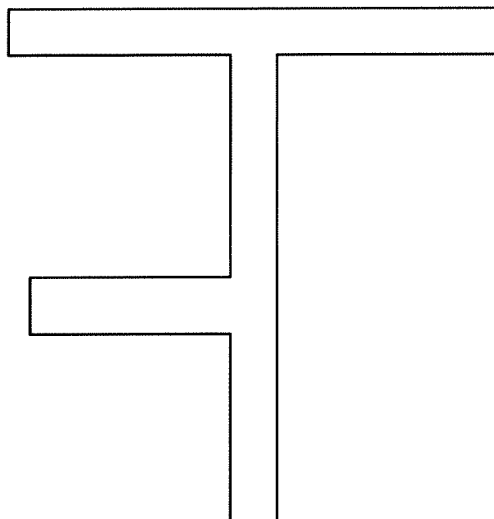
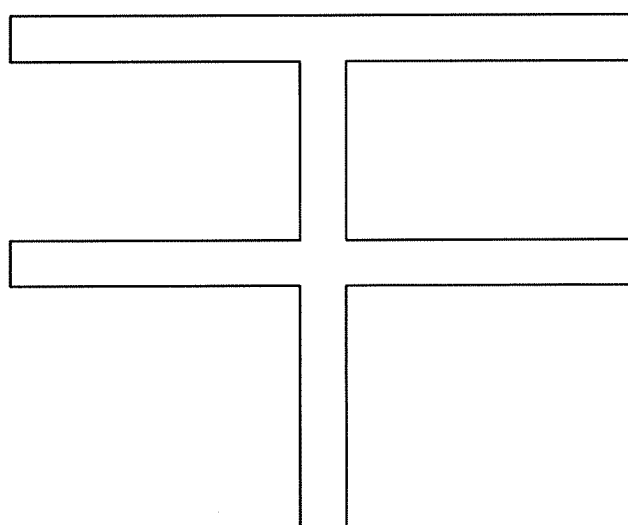


FIG. 9C



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2021/048734

A. CLASSIFICATION OF SUBJECT MATTER

C22C 14/00(2006.01)i; **B21C 23/00**(2006.01)i; **B21C 35/03**(2006.01)i
FI: C22C14/00 Z; B21C35/03; B21C23/00 A

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; B21C35/00-35/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2018-154922 A (NIPPON STEEL & SUMITOMO METAL CORP) 04 October 2018 (2018-10-04) claims, paragraphs [0026], [0030], [0031], [0033]-[0097], fig. 1-5	1-6, 8
Y		1-7
A		9-12
X	JP 2019-167621 A (NIPPON STEEL CORP) 03 October 2019 (2019-10-03) claims, paragraphs [0009], [0023], [0028]-[0094], fig. 1-5	1-7
Y		1-7
A		8-12
A	WO 2020/213719 A1 (NIPPON STEEL CORP) 22 October 2020 (2020-10-22) entire text	9-12

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

* Special categories of cited documents:

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

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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

“&” document member of the same patent family

Date of the actual completion of the international search

01 March 2022

Date of mailing of the international search report

15 March 2022

Name and mailing address of the ISA/JP

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

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2021/048734

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP	2018-154922	A	04 October 2018	(Family: none)	
JP	2019-167621	A	03 October 2019	(Family: none)	
WO	2020/213719	A1	22 October 2020	CN 113165032 A entire text KR 10-2021-0080520 A	

REFERENCES CITED IN THE DESCRIPTION

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- JP 6058535 B [0018]
- JP 2011137204 A [0018]