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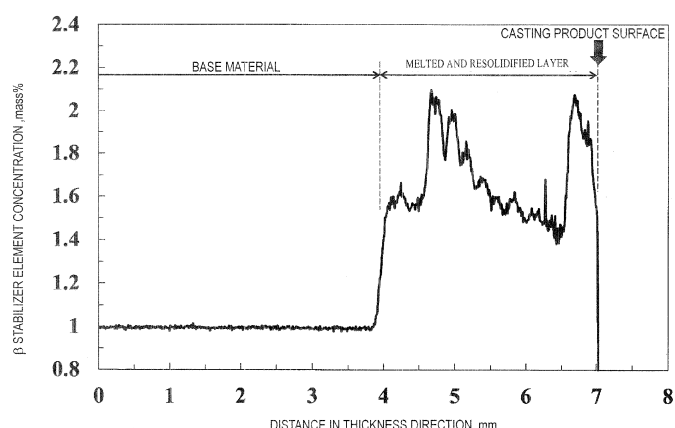
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(54) **TITANIUM SLAB FOR HOT ROLLING, AND PRODUCTION METHOD THEREFOR**

(57) Provided is a titanium cast product made of titanium alloy, the titanium cast product being produced by electron-beam remelting or plasma arc remelting, comprising: a melted and resolidified layer in a range of 1 mm or more in depth at a surface serving as a surface to be rolled, the melted and resolidified layer being obtained by adding one or more kinds of  $\beta$  stabilizer elements to the surface and melting and resolidifying the

surface. An average value of  $\beta$  stabilizer element concentration in a range of within 1 mm in depth is higher than  $\beta$  stabilizer element concentration in a base material by, in mass%, equal to or more than 0.08 mass% and equal to or less than 1.50 mass%. As the material containing the  $\beta$  stabilizer element, powder, a chip, wire, or foil is used. As means for melting a surface layer, electron-beam heating and plasma arc heating are used.

**FIG.1**



## Description

## Technical Field

**[0001]** The present invention relates to a method for producing a titanium cast product for hot rolling made of titanium alloy, particularly to a titanium cast product that can keep excellent surface properties after hot rolling even when a breakdown process such as slabbing, forging, or the like is omitted and a method for producing the same.

## Background Art

**[0002]** In general, titanium material uses titanium sponge or titanium scrap as a raw material. It is melted by non-consumable electrode arc remelting, electron-beam remelting, plasma arc remelting, or the like into a titanium ingot (titanium cast product). Non-consumable arc remelting uses titanium sponge pressed into a briquette as an electrode, and causes arc discharge between the electrode and a mold to melt the electrode itself and cast it into the mold, thereby obtaining an ingot. Therefore, uniform discharge between the electrode and the mold is necessary, which limits the shape of the mold to a cylindrical shape; accordingly, the shape of the ingot after casting is a cylindrical shape. On the other hand, electron-beam remelting and plasma arc remelting, which use electron beams and plasma arc, respectively, differ in melting method, but both the methods pour molten titanium melted on a hearth into a mold, and this allows free selection of the shape of the mold; thus, it is possible to produce ingots with various shapes, such as a rectangular shape and a billet shape, as well as a cylindrical shape.

**[0003]** In the current titanium material production process, after this, a hot working process, such as slabbing or forging, which is called an ingot breakdown process, is carried out and then hot rolling is performed; the breakdown process is necessary. However, according to the shapes, it is considered that the breakdown process can be omitted in producing a sheet material for a rectangular ingot (slab) and in producing a bar or a wire rod for a cylindrical ingot and a billet ingot, and a technology of performing hot rolling without the breakdown process has been under study. If this technology is established, it can be expected that cost will be improved by omission of a process and an enhancement in yield.

**[0004]** However, a titanium cast product produced by electron-beam remelting or plasma arc remelting is as-cast and therefore comprises coarse grains with sizes as large as several tens of millimeters. In regard to such a titanium cast product, when hot rolling is performed without a breakdown process, because of the coarse grains, the influence of deformation anisotropy in a grain and between crystal grains causes surface unevenness, leading to surface defects. In order to remove surface defects that occur in hot rolling, it is necessary to increase the amount of pickling of the surface of a hot-rolled material in a pickling process, which is the following process, and accordingly yield is worsened and may result in an increase in cost.

**[0005]** Accordingly, for a titanium ingot produced by electron-beam remelting or plasma arc remelting, while it is expected that cost will be improved by omission of a breakdown process carried out by slabbing, forging, or the like, there is a concern that an increase in surface defects may cause an increase in cost. This has inhibited practical utilization of a titanium cast product obtained without a breakdown process.

**[0006]** Patent Literature 1 discloses a method that provides an excellent casting surface and can improve surface defects after hot rolling even when an ingot breakdown process is omitted in the following case: in a cross-sectional microstructure of a titanium slab produced in an electron-beam remelting furnace and extracted directly from a mold, an angle  $\theta$  formed by the solidification direction from the surface layer toward the interior and the casting direction of the slab is in the range of 45 to 90°, or in the crystal orientation distribution of the surface layer, an angle formed by the c-axis of  $\alpha$ -Ti and the normal to the slab surface layer is in the range of 35 to 90°. That is, controlling the shape and crystal orientation of crystal grains of the surface suppresses occurrence of defects due to coarse crystal grains.

**[0007]** In Patent Literature 2, as a method for directly performing hot rolling without an ingot breakdown process for a titanium material, the surface layer at a surface corresponding to a surface to be rolled is subjected to melting and resolidification by high-frequency induction heating, arc heating, plasma heating, electron-beam heating, laser heating, and the like; thus, a portion from the surface layer to a depth of 1 mm or more undergoes grain refining. This slab surface layer is quenched and solidified to have fine and irregular crystal orientation distribution, which prevents occurrence of surface defects.

## Citation List

## Patent Literature

**[0008]**

Patent Literature i: WO/2010/090353

Patent Literature 2: JP 2007-332420A

## Summary of Invention

### Technical Problem

**[0009]** The present invention provides a titanium cast product and a method for producing the same, where the titanium cast product is obtained without any need of either a cutting and conditioning process for an as-cast titanium cast product surface layer or any breakdown process and the occurrence of the surface defects is suppressed in a titanium material after subsequent hot rolling.

### Solution to Problem

**[0010]** The present inventors carried out extensive studies in order to achieve the object. The resulting findings are as follows. When an as-cast titanium cast product produced by electron-beam remelting or plasma arc remelting, as a method for melting a titanium cast product made of titanium alloy, is subjected to hot rolling without a breakdown process, which has been conventionally necessary, a material (powder, a chip, wire, or foil) containing a  $\beta$  stabilizer element is placed or applied on the surface layer at a surface to be rolled of the as-cast titanium cast product, and the surface layer of a titanium material is melted with the material as a pre-process of hot rolling. In this manner, a layer having a higher  $\beta$  stabilizer element concentration than a base material, i.e., a  $\beta$  stabilizer element-rich layer, is formed in the surface layer of the titanium material. This makes it possible to keep excellent surface properties after hot rolling.

**[0011]** That is, the present invention is as described below.

(1) A titanium cast product for hot rolling, the titanium cast product being made of titanium alloy, comprising:

a melted and resolidified layer in a range of 1 mm or more in depth at a surface serving as a surface to be rolled, the melted and resolidified layer being obtained by adding one or more kinds of  $\beta$  stabilizer elements to the surface and melting and resolidifying the surface, wherein an average value of  $\beta$  stabilizer element concentration in a range of within 1 mm in depth is higher than  $\beta$  stabilizer element concentration in a base material by, in mass%, equal to or more than 0.08 mass% and equal to or less than 1.50 mass%.

(2) The titanium cast product for hot rolling according to (1), wherein the  $\beta$  stabilizer element(s) is/are one or more of Fe, Ni, and Cr.

(3) The titanium cast product for hot rolling according to (1), containing one or more kinds of a stabilizer element or neutral elements together with the  $\beta$  stabilizer element(s).

(4) A method for producing a titanium cast product for hot rolling, comprising:

melting a surface serving as a surface to be rolled of a titanium cast product made of titanium alloy together with a material containing a  $\beta$  stabilizer element and then solidifying the surface.

(5) The method for producing a titanium cast product for hot rolling according to (4), wherein the material containing the  $\beta$  stabilizer element is in a form of any of powder, a chip, wire, and foil.

(6) The method for producing a titanium cast product for hot rolling according to (4), wherein the surface serving as the surface to be rolled of the titanium cast product made of titanium alloy is melted by electron-beam heating or plasma heating.

### Advantageous Effects of Invention

**[0012]** With a titanium cast product according to the present invention, even when hot rolling is performed without a breakdown process such as slabbing, forging, or the like, which has been conventionally necessary, a titanium material having surface properties equivalent to those of a conventional material can be produced. A reduction in heating time due to omission of the breakdown process, a reduction in cutting treatment achieved by smoothing of the surface layer of the titanium cast product due to surface layer melting, a reduction in the amount of in pickling due to an enhancement in surface properties of the titanium material after hot rolling, and the like lead to an enhancement in yield, producing an effect of reducing production cost; the present invention offers a great effect in industry.

## Brief Description of Drawings

[0013] [FIG. 1] FIG. 1 schematically shows a change in concentration of a melted and resolidified layer.

## Description of Embodiments

[0014] Hereinafter, the present invention will be described in detail.

[0015] In general, titanium alloy is subjected to hot rolling and cold rolling, so that a sheet material, a wire rod, a bar, or the like is produced. In the present invention, titanium alloy refers to  $\alpha$  titanium alloy and  $\alpha+\beta$  titanium alloy.

[0016] Titanium cast products of interest in the present invention include rectangular ingots (slab), cylindrical ingots, and billet ingots. The surface layer of a titanium cast product with such a shape is melted together with a material containing a  $\beta$  stabilizer element, so that surface defects are suppressed for a titanium material after hot rolling.

[0017] In the present invention, only a surface layer part of an as-cast titanium cast product is heated to be melted 1 mm or more in depth. The surface layer part of the titanium cast product melted in this manner is quenched and resolidified after melting, and a cross-sectional microstructure of a melted and resolidified layer cooled to room temperature (a solidified layer that is obtained by melting only a surface layer part of an as-cast titanium cast product by heating and then performing quenching and resolidification in this manner is called a "melted and resolidified layer") is a fine acicular microstructure or a martensite microstructure. Moreover, in melting the surface layer, a base material is melted concurrently with a  $\beta$  stabilizer element; thus, the  $\beta$  stabilizer element concentration in the melted and resolidified layer becomes higher than that in the base material, and consequently, an enhancement in hardenability due to the addition of the  $\beta$  stabilizer element causes  $\alpha$  transformation or martensite transformation during cooling and thus makes the melted and resolidified layer have an even finer microstructure. The "enhancement in hardenability" here refers to low temperature  $\alpha$  transformation or martensite transformation achieved by shifting the nose of transformation in continuous cooling to the long-time side by containing the  $\beta$  stabilizer element in the surface layer of the titanium cast product. The purpose of the low temperature transformation is to increase nucleation sites to make crystal grains finer.

[0018] Furthermore, the titanium cast product subjected to the above-described melting and resolidification has high  $\beta$  stabilizing ability in the melted and resolidified layer, which brings the interior of the melted and resolidified layer into the state of  $\alpha+\beta$  region in heating for hot rolling. Since there exist two phases of  $\alpha$  phase and  $\beta$  phase, grain growth is suppressed, so that fine crystal grains after the melting and resolidification can maintain the fine grains until hot rolling after heating for hot rolling. Accordingly, unevenness of the surface of the titanium material due to coarse crystal grains can be suppressed, and thus a titanium hot-rolled material without surface defects can be produced.

[0019] As will be described in detail later, in the present invention, the formed melted and resolidified layer includes a deep portion and a shallow portion. In the present invention, the specified depth of the melted and resolidified layer is 1 mm or more; this depth refers to the depth of the shallowest portion as viewed in a cross-section in a direction perpendicular to a scanning direction of a molten bead.

[0020] When the surface layer of the titanium cast product is remelted 1 mm or more in depth as described above and then solidified, a portion from the surface layer to a depth of 1 mm or more has a fine acicular microstructure or a martensite microstructure, whereas the center side in the sheet thickness direction of the titanium material with respect to the melted and resolidified layer and a portion thermally influenced thereby keeps the microstructure as-cast. In the present invention, at least the surface layer corresponding to a surface to be rolled of the titanium cast product is remelted together with a material containing a  $\beta$  stabilizer element and then solidified, so that the average value of concentrations of the  $\beta$  stabilizer element in a portion from the surface layer to a depth of 1 mm in the melted and resolidified layer is higher than the  $\beta$  stabilizer element concentration in the base material by a certain amount. Even if melting and resolidification treatment is performed without adding a  $\beta$  stabilizer element,  $\alpha+\beta$  titanium alloy containing a P stabilizer element in its alloy composition has the effect of making crystal grains of the melted and resolidified layer finer. In this treatment, however, in the composition of a molten portion in the melting and resolidification treatment, when the surface layer is melted together with a  $\beta$  stabilizer element, solidification starts immediately after the melting, and thus sufficient diffusion does not occur in the molten portion, so that ununiformity of  $\beta$  stabilizer element concentration remains. Such remaining ununiformity causes a region with high  $\beta$  stabilizer element concentration, which makes the microstructure even finer. Moreover, in the case where the base material is remelted as it is, even if a fine microstructure is obtained in melting and resolidification, a colony, which is an aggregate of crystal grains having the same crystal orientation, may be formed. Because of the same crystal orientation, such a colony behaves like a coarse grain. Accordingly, this may lead to hot rolling defects due to the influence of deformation anisotropy. However, with the ununiformity of  $\beta$  stabilizer element concentration, the difference in  $\beta$  stabilizer element concentration creates fine crystal grains locally as described above, which suppresses occurrence of the colony and suppresses growth of the colony in heating for hot rolling. The average value of concentrations of the  $\beta$  stabilizer element in a portion from the surface layer to a depth of 1 mm in the melted and resolidified layer is higher than the  $\beta$  stabilizer element concentration in the base material by, in mass%, equal to or more than 0.08 mass% and equal to or less than 1.50 mass%. As the  $\beta$  stabilizer element, a plurality of  $\beta$  stabilizer

elements may be added in combination, in which case the  $\beta$  stabilizer element concentration refers to the sum of the concentrations of the contained  $\beta$  stabilizer elements. Since an effect is obtained by only adding the  $\beta$  stabilizer element to make the base material and the melted and resolidified layer have a difference in  $\beta$  stabilizer element concentration of 0.08 mass% or more, this value is set as a lower limit. In order to further exert the effect of suppressing surface defects, the  $\beta$  stabilizer element concentration difference preferably exceeds 0.2 mass%, and it is most preferable that the  $\beta$  stabilizer element difference exceed 0.5 mass%. Moreover, when the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer is within the aforementioned range, the  $\beta$  stabilizer element-enriched layer at the surface layer is removed by shot blasting and pickling, which are processes after hot rolling, and the  $\beta$  stabilizer element enriched in the melted and resolidified layer is detoxified. That is, the processes of shot blasting and pickling removes the  $\beta$  stabilizer element-enriched layer, making it possible to obtain components and mechanical properties equivalent to those of a cold-rolled sheet produced by a normal method. However, if the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer is more than 1.50 mass%, the volume fraction of the  $\beta$  phase, which undergoes significant oxidation, in the surface layer of the titanium cast product increases, so that the amount of oxidation increases greatly as compared with the base material. Furthermore, a difference in hot deformation resistance increases between the melted and resolidified layer at the surface layer of the titanium cast product and the base material in hot rolling, which may cause crack or the like in the surface layer or this boundary portion. These causes make it necessary to increase the amount of scarfing of the surface in a pickling process, which significantly reduces yield. In addition, it becomes difficult to detoxify the  $\beta$  stabilizer element-enriched layer in a post-process. Hence, the average value of concentrations of the  $\beta$  stabilizer element in a portion from the surface layer to a depth of 1 mm may be made to differ from the  $\beta$  stabilizer element concentration in the base material by 1.50 mass% or less. In addition, although the specified melting depth is 1 mm or more, too deep melting depth may cause the  $\beta$  stabilizer element-enriched layer to remain after the processes of shot blasting and pickling; hence, it is desirable that the melting depth be approximately 5 mm or less.

**[0021]** Moreover, normally, a titanium cast product in casting undergoes solidification from a surface layer part of the titanium cast product in contact with the mold; therefore, components slightly differ between the surface layer and the interior of the titanium cast product depending on distribution of a solute for each element. Since a  $\beta$ -stabilizer, such as Fe, exhibits normal segregation, in solidification or in transformation, the Fe concentration in the surface layer part of the titanium cast product decreases and the Fe concentration tends to become higher toward the interior of the titanium cast product. Therefore, it is very effective to make the  $\beta$ -stabilizer concentration in the melted and resolidified layer equal to or higher than that in the parent metal by melting the  $\beta$ -stabilizer and the parent metal concurrently. This effect is especially significant with  $\alpha$  titanium alloy.

**[0022]** In addition, in casting of the titanium material, components are adjusted to be uniform in the entire slab by controlling input of raw materials. However, fluctuation of components or the like may occur partially. Therefore, in an alloy originally having a low  $\beta$ -stabilizer concentration, a region may exist in which crystal grains are not sufficiently fine in the melted and resolidified layer, according to component fluctuation of the  $\beta$ -stabilizer, and surface defects may occur partially after hot rolling. Hence, it is effective to add a  $\beta$ -stabilizer in melting and resolidification to raise the amount of the  $\beta$ -stabilizer added; thus, partial surface defects can also be suppressed. In addition, as mentioned above, component fluctuation of the  $\beta$ -stabilizer in the melted and resolidified phase is greater than component fluctuation in the parent metal also in an alloy originally having a high  $\beta$ -stabilizer concentration; thus, the effect of splitting a colony further increases, making it possible to suppress partial surface defects.

**[0023]** In a cross-section in a direction perpendicular to a scanning direction of a molten bead, the melted and resolidified layer tends to be deepest at the center of the molten bead in remelting of the surface layer of the titanium cast product, and, when molten beads are overlapped, is shallowest at a portion midway between adjacent molten beads, the deepest portion and the shallowest portion being repeated periodically. Here, if a difference between the deepest portion and the shallowest portion is large, this difference causes a difference in deformation resistance in hot rolling, which may cause defects. Hence, it is desirable that the above difference be less than 2 mm. Note that in the present invention, the specified depth of the melted and resolidified layer is 1 mm or more; this depth refers to the depth of the shallowest portion as viewed in a cross-section in a direction perpendicular to a scanning direction of a molten bead.

**[0024]** Description will be given on a method for measuring the depth of the melted and resolidified layer and uniformity in melting and resolidification. A portion cut out from the surface layer portion of the titanium cast product in a cross-section in a direction perpendicular to a scanning direction of a molten bead is used as an embedding and polishing sample for scanning electron microscopy (SEM)/ an electron probe microanalyser (EPMA); thus, the melted and resolidified layer can be distinguished easily. In the present invention, since the depth of the melted and resolidified layer is defined as the depth of the shallowest portion, a melting depth can be simply obtained by elemental mapping analysis. FIG. 1 shows an example of measured values of changes in concentration of the parent metal and the melted and resolidified layer. This is obtained by linear analysis of  $\beta$ -stabilizer concentration in the thickness direction from a parent metal portion near the surface layer at a surface to be rolled of the titanium cast product toward the surface to be rolled. In the base material, the  $\beta$  stabilizer element concentration is low and substantially uniform, whereas in the melted and

resolidified layer, the  $\beta$  stabilizer element concentration is high and also exhibits concentration fluctuation, which indicates nonuniformity.

**[0025]** Examples of the  $\beta$  stabilizer element include V, Mo, Fe, Cr, Mn, Ta, Nb, Ni, Co, Cu, and W. In titanium, however, an element such as W or Ta having a high melting point causes high density inclusion (HDI), and serves as a starting point of fatigue when it remains in the titanium material without being melted or without being diffused sufficiently: therefore, such an element needs to be used with care. Moreover, Mo, Nb, and the like have lower melting points than W and Ta, but still have melting points of 2000°C or higher; therefore, when using Mo or Nb, it is desirable to alloy it with an element such as Ti in advance to make the melting point lower and add the resulting alloy.  $\beta$  stabilizer elements can be classified into a complete solid solution type, such as V, Mo, Ta, and Nb, and an eutectoid type, such as Fe, Cr, Mn, Co, Ni, and Cu.  $\beta$  stabilizer elements of the eutectoid type have low solid solubility but have high  $\beta$  stabilizing ability; therefore, addition of a  $\beta$  stabilizer element of the eutectoid type is effective even in a small amount. In regard to Fe, Cr, Mn, Co, Ni, and Cu, which are of the eutectoid type, surface defects after hot rolling can be suppressed when  $\beta$  stabilizer element concentration in the melted and resolidified layer is higher than that in the base material by approximately 0.10 to 0.60 mass%; hence, this range is preferable. In regard to V, Mo, Ta, and Nb, which are of the complete solid solution type, which have low  $\beta$  stabilizing ability as compared with the eutectoid type, it is desirable to add a  $\beta$  stabilizer element in a large amount such that  $\beta$  stabilizer element concentration in the melted and resolidified layer is higher than that in the base material by approximately 0.60 to 1.50 mass%. Even when a  $\beta$  stabilizer element of the eutectoid type is used, since quenching is performed in solidification after remelting, cooling rate is high and no precipitate occurs, and also in heating for hot rolling, no precipitate occurs because the state is the  $\alpha + \beta$  region. Furthermore, the material containing the  $\beta$  stabilizer element may contain a  $\alpha$ -stabilizer typified by Al, or a neutral element, such as Sn or Zr. Either one or both of a  $\alpha$ -stabilizer and a neutral element may be contained. The total amount of a  $\alpha$ -stabilizer and a neutral element in the melted and resolidified layer is preferably 2.0 mass% or less with respect to the base material. Fe, Ni, and Cr, which are relatively inexpensive  $\beta$  stabilizer elements, are preferably used as the material to be melted together with the surface layer of the as-cast titanium cast product. It is also effective to use Fe powder or the like or stainless steel powder or the like, or utilize crushed scrap of ordinary steel or stainless steel. Similarly, crushed scrap of titanium alloy may be used.

**[0026]** The material used for adding the  $\beta$  stabilizer element to the surface layer of the cast product may have any of the shapes of powder, a chip, wire, and foil, and it is desirable that the material be in a small piece. It is effective to use any of the following materials: powder with a particle size in a range of 1  $\mu\text{m}$  to 0.5 mm, a chip with a size in a range of 2 mm square to 5 mm square, wire with a diameter in a range of 0.5 mm to 5 mm, and foil with a thickness in a range of 1  $\mu\text{m}$  to 0.1 mm. Such a material is disposed uniformly on the surface of the cast product when placed or applied on the surface of the cast product; thus, it can be added uniformly to the surface layer of the titanium cast product, which provides a titanium cast product with more excellent surface properties.

**[0027]** Methods for melting the surface layer together with the  $\beta$  stabilizer element include electron-beam heating, arc heating, laser heating, and induction heating. Titanium is active metal, and when the surface layer is melted in atmospheric air, a molten portion is oxidized significantly. Hence, the following methods are suitable: electron-beam heating, arc heating (in particular, a heating method using inert gas, such as plasma arc heating or tungsten inert gas (TIG) welding), laser heating, and the like, which can perform treatment in a vacuum atmosphere or an inert gas atmosphere. The aforementioned treatment can be performed by any of these methods. Of these, electron-beam heating or plasma arc heating, which can apply high energy at once, is suitable for industry and preferred to be used.

[Examples]

**[0028]** Hereinafter, the present invention will be described in more detail in Examples.

[Table 1]

| No. | Grade                    | Difference in $\beta$ stabilizer element concentration (mass%)<br>between base material and melted and resolidified layer (surface layer 1 mm) |      |      |      |      |      |      |      |      |      |      | Melting method | Depth of<br>melted and<br>resolidified layer<br>(mm) | Slabbing | Ingot cutting<br>treatment | Surface defects | Evaluation                        | Remarks |                     |
|-----|--------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|------|------|------|------|------|------|------|------|------|------|----------------|------------------------------------------------------|----------|----------------------------|-----------------|-----------------------------------|---------|---------------------|
|     |                          | All $\beta$ stabilizer elements                                                                                                                |      |      |      |      |      |      |      |      |      |      |                |                                                      |          |                            |                 |                                   |         |                     |
|     |                          | Form of additive                                                                                                                               | Fe   | Cr   | Ni   | Mo   | V    | Mn   | Co   | Cu   | Nb   | Or   |                |                                                      |          |                            |                 |                                   |         |                     |
| 1   | Ti-1Fe-0.350             | none                                                                                                                                           | 0.00 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.00           | none                                                 | 0        | Yes                        | Yes             | minor                             | Good    | Reference Example   |
| 2   | Ti-1Fe-0.350             | none                                                                                                                                           | 0.00 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.00           | none                                                 | 0        | No                         | Yes             | coarse defects                    | Fair    | Comparative Example |
| 3   | Ti-1Fe-0.350             | none                                                                                                                                           | 0.20 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.00           | electron beam                                        | 2        | No                         | Yes             | partially somewhat coarse defects | Fair    | Comparative Example |
| 4   | Ti-1Fe-0.350             | Fe powder                                                                                                                                      | 0.26 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.26           | electron beam                                        | 0.5      | No                         | Yes             | partially somewhat coarse defects | Fair    | Comparative Example |
| 5   | Ti-1Fe-0.350             | Fe powder                                                                                                                                      | 0.83 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.83           | electron beam                                        | 3        | No                         | Yes             | minor                             | Good    | Example             |
| 6   | Ti-1Fe-0.350             | Fe powder                                                                                                                                      | 1.50 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 1.50           | electron beam                                        | 5        | No                         | No              | minor                             | Good    | Example             |
| 7   | Ti-1Fe-0.350             | Fe powder                                                                                                                                      | 0.42 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.42           | plasma arc                                           | 4        | No                         | No              | minor                             | Good    | Example             |
| 8   | Ti-1Fe-0.350             | Fe chip                                                                                                                                        | 0.08 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.08           | electron beam                                        | 1        | No                         | No              | minor                             | Good    | Example             |
| 9   | Ti-1Fe-0.350             | Fe wire                                                                                                                                        | 0.87 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.87           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 10  | Ti-1Fe-0.350             | Fe foil                                                                                                                                        | 1.22 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 1.22           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 11  | Ti-1Fe-0.350             | Cr chip                                                                                                                                        | 0.00 | 0.51 | —    | —    | —    | —    | —    | —    | —    | —    | 0.51           | electron beam                                        | 3        | No                         | No              | minor                             | Good    | Example             |
| 12  | Ti-1Fe-0.350             | Ni chip                                                                                                                                        | 0.00 | —    | 0.33 | —    | —    | —    | —    | —    | —    | —    | 0.38           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 13  | Ti-1Fe-0.350             | Ti-Mo chip                                                                                                                                     | 0.00 | —    | —    | 1.36 | —    | —    | —    | —    | —    | —    | 1.38           | electron beam                                        | 4        | No                         | No              | minor                             | Good    | Example             |
| 14  | Ti-1Fe-0.350             | V chip                                                                                                                                         | 0.00 | —    | —    | —    | 1.03 | —    | —    | —    | —    | —    | 1.03           | electron beam                                        | 5        | No                         | No              | minor                             | Good    | Example             |
| 15  | Ti-1Fe-0.350             | Mn chip                                                                                                                                        | 0.00 | —    | —    | —    | —    | 0.14 | —    | —    | —    | —    | 0.14           | electron beam                                        | 3        | No                         | No              | minor                             | Good    | Example             |
| 16  | Ti-1Fe-0.350             | Co chip                                                                                                                                        | 0.00 | —    | —    | —    | —    | —    | 0.86 | —    | —    | —    | 0.86           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 17  | Ti-1Fe-0.350             | Cu chip                                                                                                                                        | 0.00 | —    | —    | —    | —    | —    | 0.57 | —    | —    | —    | 0.57           | electron beam                                        | 1        | No                         | No              | minor                             | Good    | Example             |
| 18  | Ti-1Fe-0.350             | Fe-Nb chip                                                                                                                                     | 0.11 | —    | —    | —    | —    | —    | —    | 0.21 | —    | —    | 0.32           | electron beam                                        | 4        | No                         | No              | minor                             | Good    | Example             |
| 19  | Ti-1Fe-0.350             | SUS304 powder                                                                                                                                  | 0.44 | 0.11 | 0.05 | —    | —    | —    | —    | —    | —    | —    | 0.60           | electron beam                                        | 1        | No                         | No              | minor                             | Good    | Example             |
| 20  | Ti-1Fe-0.350             | 5-4 chip                                                                                                                                       | 0.00 | —    | —    | —    | 0.29 | —    | —    | —    | —    | —    | 0.20           | electron beam                                        | 3        | No                         | No              | minor                             | Good    | Example             |
| 21  | Ti-1Fe-0.350             | 15-3-3-3 chip                                                                                                                                  | 0.00 | —    | —    | —    | 0.82 | —    | —    | —    | 0.16 | —    | 0.48           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 22  | Ti-0.06Pd                | Fe powder                                                                                                                                      | 0.68 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.68           | electron beam                                        | 4        | No                         | No              | minor                             | Good    | Example             |
| 23  | Ti-0.38Al-0.03Pd         | Fe powder                                                                                                                                      | 0.59 | —    | 0.00 | —    | —    | —    | —    | —    | —    | —    | 0.59           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 24  | Ti-5Al-1Fe               | Fe powder                                                                                                                                      | 0.31 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.31           | electron beam                                        | 4        | No                         | No              | minor                             | Good    | Example             |
| 25  | Ti-5Al-1Fe-0.25Sn        | Fe powder                                                                                                                                      | 0.12 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.12           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 26  | Ti-5Al-2.5V              | Fe powder                                                                                                                                      | 0.17 | —    | —    | —    | 0.00 | —    | —    | —    | —    | —    | 0.17           | electron beam                                        | 3        | No                         | No              | minor                             | Good    | Example             |
| 27  | Ti-0.50Cu                | Fe powder                                                                                                                                      | 0.11 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.12           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 28  | Ti-1Cu                   | Fe powder                                                                                                                                      | 0.72 | —    | —    | —    | —    | —    | —    | —    | 0.00 | —    | 0.11           | electron beam                                        | 3        | No                         | No              | minor                             | Good    | Example             |
| 29  | Ti-1Cu-0.5Nb             | Fe powder                                                                                                                                      | 0.55 | —    | —    | —    | —    | —    | —    | —    | 0.00 | 0.00 | 0.55           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 30  | Ti-1Cu-13Fe-0.35Sn-0.2Nb | Fe powder                                                                                                                                      | 0.64 | —    | —    | —    | —    | —    | —    | —    | 0.00 | 0.00 | 0.64           | electron beam                                        | 1        | No                         | No              | minor                             | Good    | Example             |
| 31  | Ti-3Al-5V                | Fe powder                                                                                                                                      | 0.22 | —    | —    | —    | —    | 0.00 | —    | —    | —    | —    | 0.22           | electron beam                                        | 3        | No                         | No              | minor                             | Good    | Example             |
| 32  | Ti-3Al-2.5V              | none                                                                                                                                           | 0.00 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.00           | none                                                 | 0        | Yes                        | Yes             | coarse defects                    | Good    | Reference Example   |
| 33  | Ti-3Al-2.5V              | none                                                                                                                                           | 0.00 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.00           | none                                                 | 0        | No                         | Yes             | coarse defects                    | Fair    | Comparative Example |
| 34  | Ti-3Al-2.5V              | none                                                                                                                                           | 0.00 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.00           | electron beam                                        | 2        | No                         | Yes             | partially somewhat coarse defects | Fair    | Comparative Example |
| 35  | Ti-3Al-2.5V              | Fe foil                                                                                                                                        | 0.52 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.52           | electron beam                                        | 0.5      | No                         | Yes             | partially somewhat coarse defects | Fair    | Comparative Example |
| 36  | Ti-3Al-2.5V              | Fe foil                                                                                                                                        | 0.67 | —    | —    | —    | —    | 0.00 | —    | —    | —    | —    | 0.67           | electron beam                                        | 3        | No                         | Yes             | minor                             | Good    | Example             |
| 37  | Ti-3Al-2.5V              | Fe foil                                                                                                                                        | 1.42 | —    | —    | —    | —    | 0.00 | —    | —    | —    | —    | 1.42           | electron beam                                        | 1        | No                         | No              | minor                             | Good    | Example             |
| 38  | Ti-3Al-2.5V              | Fe foil                                                                                                                                        | 0.16 | —    | —    | —    | —    | 0.00 | —    | —    | —    | —    | 0.16           | plasma arc                                           | 5        | No                         | No              | minor                             | Good    | Example             |
| 39  | Ti-3Al-2.5V              | Cr chip                                                                                                                                        | —    | 0.84 | —    | —    | —    | 0.00 | —    | —    | —    | —    | 0.84           | electron beam                                        | 4        | No                         | No              | minor                             | Good    | Example             |
| 40  | Ti-3Al-2.5V              | Ni chip                                                                                                                                        | —    | —    | 1.33 | —    | —    | 0.00 | —    | —    | —    | —    | 1.33           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |
| 41  | Ti-3Al-2.5V              | SUS304 powder                                                                                                                                  | 0.59 | 0.15 | 0.06 | —    | —    | 0.00 | —    | —    | —    | —    | 0.80           | electron beam                                        | 2        | No                         | No              | minor                             | Good    | Example             |

[0029] In each of Reference Examples, Examples, and Comparative Examples shown in Table 1, a titanium cast product was produced using a rectangular mold or a cylindrical mold made of titanium alloy of various grades by electron-beam remelting. A hot-rolled sheet with a thickness of 4 mm was produced by hot rolling from an ingot with a size of thickness 200 mm  $\times$  width 1000 mm  $\times$  length 4500 mm produced using a rectangular mold, and a wire rod with a diameter of 13 mm was produced by hot rolling from an ingot with a size of diameter 170 mm  $\times$  length 12 m produced

using a cylindrical mold. Hot rolling was performed using hot rolling equipment for steel material. As a material containing a  $\beta$  stabilizer element, any of powder (particle size: 100  $\mu\text{m}$  or less), a chip (2 mm square, 1 mm thick), wire (diameter: 1mm), and foil (20  $\mu\text{m}$ ) was used. Titanium cast products fabricated included two kinds: those not subjected to cutting treatment and those subjected to cutting treatment. In containing the  $\beta$  stabilizer element, the material containing the  $\beta$  stabilizer element was placed or applied on the as-cast surface (without cutting treatment on casting surface) or the cut surface (with cutting treatment on casting surface), both of which are surfaces to be rolled. A slab surface layer was heated from above the material, and a surface to be rolled was entirely treated by scanning a portion to be heated with electron beams and plasma arc; thus, the material containing the  $\beta$  stabilizer element and the surface to be rolled included no portion remaining unmelted. In addition, an as-cast titanium cast product with a relatively excellent casting surface was used to prevent occurrence of an unmelted portion due to the casting surface in melting of the surface layer. Moreover, the material containing the  $\beta$  stabilizer element was dispersed uniformly on the entire surface to be rolled of the titanium cast product so that the  $\beta$  stabilizer element was added uniformly to the entire slab. As a method for measuring the depth of the melted and resolidified layer, a titanium cast product obtained by remelting and then solidifying the surface layer was partly cut out and an embedding sample was fabricated and subjected to polishing for scanning electron microscopy (SEM)/ electron probe microanalyser (EPMA), and elemental mapping was performed, whereby the depth of the shallowest portion of the melted and resolidified part of the embedding sample was obtained as the depth of the melted and resolidified layer. Moreover, here, analysis samples were taken from within 1 mm of the surface layer at any ten spots of the surface to be rolled of the titanium cast product and were subjected to ICP-atomic emission spectrometry, and the average value of the ten spots was obtained. In addition, for comparison, analysis samples were taken from within 20 mm of the surface layer at any three spots of the surface to be rolled of the titanium cast product before remelting of the surface layer of the titanium cast product, and were subjected to ICP-atomic emission spectrometry similarly, and the average value of the three spots was obtained. Regarding these two kinds of analysis results, a difference between the average value of the  $\beta$  stabilizer element concentration in a range of within 1 mm in depth of the melted and resolidified layer and the average value of the  $\beta$  stabilizer element concentration in the base material was investigated. The situation of occurrence of surface defects was evaluated by visually observing the surface of the titanium material (hot-rolled sheet) after the hot-rolled sheet was subjected to shot blasting and pickling after hot rolling. Pickling was performed to scarf one side of the surface to be rolled approximately 50  $\mu\text{m}$  (approximately 100  $\mu\text{m}$  for both sides) per once. After the sheet underwent pickling once or twice, surface properties of the hot-rolled sheet were evaluated. Note that an analysis sample was taken from within 1 mm of the surface layer for Comparative Example not subjected to surface layer melting treatment, and an analysis sample was taken from the interior of the melted and resolidified layer for Comparative Example with a thickness of the melted and resolidified layer of less than 1 mm.

**[0030]** Nos. 1 to 31 were examples for sheet materials.

**[0031]** In Reference Example, Comparative Examples, and Example of Nos. 1 to 5, cutting treatment was performed on a casting surface after ingot casting to remove the casting surface, whereas in Examples of Nos. 6 to 31, cutting treatment was not performed on a casting surface after ingot casting.

**[0032]** In Reference Example, Comparative Examples, and Examples of Nos. 1 to 21, an ingot of Ti-1Fe-0.35O was used.

**[0033]** Reference Example of No. 1 was produced with slabbing performed as in a conventional production method. Because of the slabbing, surface defects that occurred in a hot-rolled sheet after pickling were minor.

**[0034]** Comparative Example of No. 2 was produced without performing slabbing after ingot cutting treatment. Because of no slabbing, coarse defects occurred in a hot-rolled sheet after pickling.

**[0035]** In Comparative Example of No. 3, melting and resolidification treatment was performed by electron-beam heating without adding a  $\beta$  stabilizer element, after ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more, and surface defects after hot rolling and pickling were basically minor, but somewhat coarse defects occurred partially.

**[0036]** In Comparative Example of No. 4, melting and resolidification treatment was performed by electron-beam heating using Fe powder as the  $\beta$  stabilizer element, after ingot cutting treatment. The melted and resolidified layer had a depth of less than 1 mm, and somewhat coarse defects occurred partially as surface defects after hot rolling and pickling.

**[0037]** In Example of No. 5, melting and resolidification treatment was performed by electron-beam heating using Fe powder as the  $\beta$  stabilizer element, after ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentrations between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

**[0038]** In Example of No. 6, melting and resolidification treatment was performed by electron-beam heating using Fe powder as the  $\beta$  stabilizer element, without performing ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.



**[0039]** In Example of No. 7, melting and resolidification treatment was performed by plasma arc heating using Fe powder as the  $\beta$  stabilizer element, without performing ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

**[0040]** In Examples of Nos. 8 to 10, melting and resolidification treatment was performed by electron-beam heating using a Fe chip, Fe wire, and Fe foil, respectively, as the  $\beta$  stabilizer element, without performing ingot cutting treatment. In each case, the melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

**[0041]** In Examples of Nos. 11 to 17, melting and resolidification treatment was performed by electron-beam heating with the kinds of  $\beta$  stabilizer elements changed by using a Cr chip, a Ni chip, a Ti-Mo chip, a V chip, a Mn chip, a Co chip, and a Cu chip as the  $\beta$  stabilizer element, without performing ingot cutting treatment. In each case, the melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

**[0042]** In Examples of Nos. 18 to 21, melting and resolidification treatment was performed by electron-beam heating using materials containing several kinds of  $\beta$  stabilizer elements and a stabilizer elements of a Fe-Nb chip, SUS304 powder, a chip (6-4V chip) obtained by crushing Ti-6mass%Al-4mass%V scrap, and a chip (15-3-3-3 chip) obtained by crushing Ti-15mass%V-3mass%Cr-3mass%Sn-3mass%Al scrap, respectively, as the  $\beta$  stabilizer element, without performing ingot cutting treatment. In each case, the melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

**[0043]** In Examples of Nos. 22 to 31, the kinds of titanium alloy ingots were changed. No. 22 used Ti-0.06mass%Pd, No. 23 used Ti-0.5mass%Ni-0.05mass%Ru, No. 24 used Ti-5mass%Al-1mass%Fe, No. 25 used Ti-5mass%Al-1mass%Fe-0.25mass%Si, No. 26 used Ti-3mass%Al-2.5mass%V, No. 27 used Ti-0.5mass%Cu, No. 28 used Ti-1mass%Cu, No. 29 used titanium alloy of Ti-1mass%Cu-0.5mass%Nb, No. 30 used Ti-1mass%Cu-1mass%Sn-0.3mass%Si-0.2mass%Nb, and No. 31 used Ti-3mass%Al-5mass%V. In each case, melting and resolidification treatment was performed by electron-beam heating using Fe powder as the  $\beta$  stabilizer element, without performing ingot cutting treatment. In each case, the melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

**[0044]** Nos. 32 to 41 were examples for wire rods.

**[0045]** In Reference Example, Comparative Examples, and Example of Nos. 32 to 36, cutting treatment was performed on a casting surface after ingot casting to remove the casting surface, whereas in Examples of Nos. 37 to 41, cutting treatment was not performed on a casting surface after ingot casting.

**[0046]** In Reference Example, Comparative Examples, and Examples of Nos. 32 to 41, an ingot of Ti-3mass%Al-2.5mass%V was used.

**[0047]** Reference Example of No. 32 was produced with slabbing performed as in a conventional production method. Because of the slabbing, surface defects that occurred in a hot-rolled sheet after pickling were minor.

**[0048]** Comparative Example of No. 33 was produced without performing slabbing after ingot cutting treatment. Because of no slabbing, coarse defects occurred in a hot-rolled sheet after pickling.

**[0049]** In Comparative Example of No. 34, melting and resolidification treatment was performed by electron-beam heating without adding a  $\beta$  stabilizer element, after ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more, and surface defects after hot rolling and pickling were basically minor, but somewhat coarse defects occurred partially.

**[0050]** In Comparative Example of No. 35, melting and resolidification treatment was performed by electron-beam heating using Fe foil as the  $\beta$  stabilizer element, after ingot cutting treatment. The melted and resolidified layer had a depth of less than 1 mm, and somewhat coarse defects occurred partially as surface defects after hot rolling and pickling.

**[0051]** In Example of No. 36, melting and resolidification treatment was performed by electron-beam heating using Fe foil as the  $\beta$  stabilizer element, after ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

**[0052]** In Example of No. 37, melting and resolidification treatment was performed by electron-beam heating using Fe foil as the  $\beta$  stabilizer element, without performing ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and

resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

[0053] In Example of No. 38, melting and resolidification treatment was performed by plasma arc heating using Fe foil as the  $\beta$  stabilizer element, without performing ingot cutting treatment. The melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

[0054] In Examples of Nos. 39 and 40, melting and resolidification treatment was performed by electron-beam heating with the kinds of  $\beta$  stabilizer elements changed by using a Cr chip and a Ni chip as the  $\beta$  stabilizer element, without performing ingot cutting treatment. In each case, the melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

[0055] In Example of No. 41, melting and resolidification treatment was performed by electron-beam heating using SUS304 powder containing a plurality of  $\beta$  stabilizer elements as the  $\beta$  stabilizer element, without performing ingot cutting treatment. In each case, the melted and resolidified layer had a depth of 1 mm or more and the difference in  $\beta$  stabilizer element concentration between the base material and the melted and resolidified layer was equal to or more than 0.08 mass% and equal to or less than 1.50 mass%, and surface defects after hot rolling and pickling were minor.

## Claims

1. A titanium cast product for hot rolling, the titanium cast product being made of titanium alloy, comprising:

a melted and resolidified layer in a range of 1 mm or more in depth at a surface serving as a surface to be rolled, the melted and resolidified layer being obtained by adding one or more kinds of  $\beta$  stabilizer elements to the surface and melting and resolidifying the surface,

wherein an average value of  $\beta$  stabilizer element concentration in a range of within 1 mm in depth is higher than  $\beta$  stabilizer element concentration in a base material by, in mass%, equal to or more than 0.08 mass% and equal to or less than 1.50 mass%.

2. The titanium cast product for hot rolling according to claim 1, wherein the  $\beta$  stabilizer element(s) is/are one or more of Fe, Ni, and Cr.

3. The titanium cast product for hot rolling according to claim 1, containing one or more kinds of  $\alpha$  stabilizer elements or neutral elements together with the  $\beta$  stabilizer element(s).

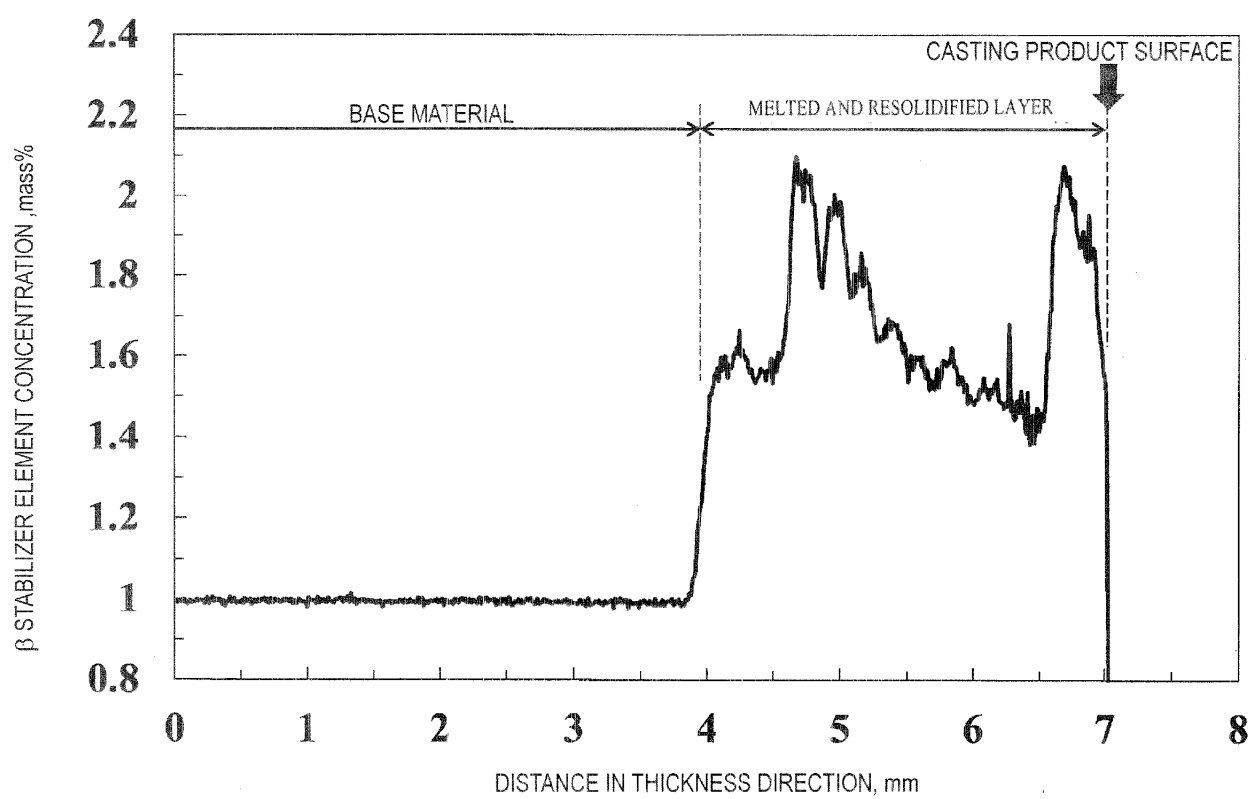
4. A method for producing a titanium cast product for hot rolling, comprising:

melting a surface serving as a surface to be rolled of a titanium cast product made of titanium alloy together with a material containing a  $\beta$  stabilizer element and then solidifying the surface.

5. The method for producing a titanium cast product for hot rolling according to claim 4, wherein the material containing the  $\beta$  stabilizer element is in a form of any of powder, a chip, wire, and foil.

6. The method for producing a titanium cast product for hot rolling according to claim 4, wherein the surface serving as the surface to be rolled of the titanium cast product made of titanium alloy is melted by electron-beam heating or plasma heating.

FIG.1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/076083

## A. CLASSIFICATION OF SUBJECT MATTER

C23C26/00(2006.01)i, B21B1/02(2006.01)i, B21B3/00(2006.01)i, B22D21/06  
(2006.01)i, B22D29/00(2006.01)i, C22C14/00(2006.01)i

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C26/00, B21B1/02, B21B3/00, B22D21/06, B22D29/00, C22C14/00

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014  
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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 2007-332420 A (Nippon Steel Corp.),<br>27 December 2007 (27.12.2007),<br>claims; paragraphs [0001] to [0011], [0025] to<br>[0046]<br>(Family: none) | 1-6                   |
| A         | JP 09-314278 A (Fukushima Steel Works Co.,<br>Ltd.),<br>09 December 1997 (09.12.1997),<br>paragraph [0003]<br>(Family: none)                           | 1-6                   |
| E, X      | WO 2014/163087 A1 (Nippon Steel & Sumitomo<br>Metal Corp.),<br>09 October 2014 (09.10.2014),<br>claims 4 to 6<br>(Family: none)                        | 4-6                   |

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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Date of the actual completion of the international search  
12 December, 2014 (12.12.14)

Date of mailing of the international search report  
22 December, 2014 (22.12.14)

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**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- WO 2010090353 A [0008]
- JP 2007332420 A [0008]