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(54) TITANIUM SINTERED BODY AND ORNAMENT

(57) A titanium sintered body contains an α-phase and a β-phase as crystal structures, wherein the average grain size of the α-phase in a cross section is 3 μm or more and 30 μm or less, and an area ratio occupied by the α-phase in a cross section is 70% or more and 99.8% or less. In the titanium sintered body, it is preferred that the average aspect ratio of the α-phase in a cross section is 1 or more and 3 or less. It is also preferred that the titanium sintered body contains titanium as a main component, and also contains an α-phase stabilizing element and a β-phase stabilizing element.

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Description

BACKGROUND

1. Technical Field

[0001] The present invention relates to a titanium sintered body and an ornament.

2. Related Art

[0002] A titanium alloy has excellent mechanical strength and corrosion resistance, and therefore has been used in the field of aircraft, space development, chemical plants, and the like. Further, recently, by utilizing the characteristics such as biocompatibility and a low Young's modulus of a titanium alloy, a titanium alloy has begun to be applied to exterior components of watches, ornaments such as glasses frames, sporting goods such as golf clubs, springs, and the like.

[0003] Further, in the application of a titanium alloy in this manner, by using a powder metallurgy method, a titanium sintered body having a shape close to the final shape can be easily produced. Therefore, secondary processing can be omitted or a processing amount can be reduced, and thus, components can be efficiently produced.

[0004] However, a titanium sintered body produced by a powder metallurgy method is likely to reflect the properties of a starting material powder, and it is difficult to increase the surface smoothness. Due to this, the specularity of the titanium sintered body is easy to decrease, which can cause a problem of appearance.

[0005] Therefore, an attempt to improve the specularity of a titanium sintered body produced by a powder metallurgy method has been proposed.

[0006] For example, JP-A-8-92674 (PTL 1) discloses a titanium alloy for ornaments obtained by powder compacting a mixed powder containing an iron powder in an amount of 0.1 to 1.0 % by weight and a molybdenum powder in an amount of 0.1 to 4.0 % by weight with the remainder consisting of a titanium powder, followed by sintering at 1200 to 1350°C. Further, PTL 1 describes that the obtained titanium alloy contains an α+β two-phase structure, and specularity required for an external component of watches or the like is obtained.

[0007] However, the titanium alloy disclosed in PTL 1 contains iron in addition to titanium, and therefore has poor weather resistance. Due to this, in the case where the titanium alloy is exposed to a harsh environment for a long period of time, deterioration occurs on the surface, resulting in lowering the specularity.

SUMMARY

[0008] An advantage of some aspects of the invention is to provide a titanium sintered body and an ornament capable of maintaining good specularity for a long period of time.

[0009] A titanium sintered body according to an aspect of the invention contains an α-phase and a β-phase as crystal structures, wherein the average grain size of the α-phase in a cross section is 3 μm or more and 30 μm or less, and an area ratio occupied by the α-phase in a cross section is 70% or more and 99.8% or less.

[0010] With this configuration, a titanium sintered body capable of maintaining good specularity for a long period of time is obtained.

[0011] In the titanium sintered body according to the aspect of the invention, it is preferred that the average aspect ratio of the α-phase in a cross section is 1 or more and 3 or less.

[0012] With this configuration, anisotropy is less likely to occur in a polishing amount when polishing processing is performed for the titanium sintered body, and therefore, unevenness is less likely to occur on the polished surface. Due to this, the smoothness of the polished surface can be further increased, and thus, a titanium sintered body having particularly excellent specularity is obtained.

[0013] In the titanium sintered body according to the aspect of the invention, it is preferred that in an X-ray diffraction spectrum obtained by X-ray diffractometry, the value of a peak reflection intensity by the plane orientation (110) of the β-phase is 3% or more and 60% or less of the value of a peak reflection intensity by the plane orientation (100) of the α-phase.

[0014] With this configuration, both characteristics of the α-phase and characteristics of the β-phase become obvious without being buried. As a result, a titanium sintered body capable of maintaining high specularity particularly for a long period of time is obtained.

[0015] In the titanium sintered body according to the aspect of the invention, it is preferred that the titanium sintered body contains titanium as a main component, and also contains an α-phase stabilizing element and a β-phase stabilizing element.

[0016] With this configuration, even if the production conditions or use conditions for the titanium sintered body change, since the titanium sintered body can have both α-phase and β-phase as the crystal structures, the titanium sintered body has excellent weather resistance. As a result, the titanium sintered body has both characteristics exhibited by the α-phase and characteristics exhibited by the β-phase, and thus has particularly excellent mechanical properties.

[0017] In the titanium sintered body according to the aspect of the invention, it is preferred that the titanium sintered body has a relative density of 99% or more.

[0018] With this configuration, when the surface of the titanium sintered body is polished, particularly good specularity is exhibited.

[0019] An ornament according to an aspect of the invention includes the titanium sintered body according the aspect of the invention.

[0020] With this configuration, an ornament capable of maintaining good specularity for a long period of time, and as a result, capable of maintaining excellent aesthetic appearance for a long period of time is obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The invention will be described with reference to the accompanying drawings, wherein like numbers reference like elements.

FIG. 1 is an electron microscopic image showing an embodiment of a titanium sintered body according to the invention.
FIG. 2 is a view schematically drawing a part of the electron microscopic image shown in FIG. 1.
FIG. 3 is a perspective view showing a watch case to which an embodiment of an ornament according to the invention is applied.
FIG. 4 is a partial cross-sectional perspective view showing a bezel to which an embodiment of an ornament according to the invention is applied.
FIG. 5 is an X-ray diffraction spectrum obtained for a titanium sintered body of Example 1.
FIG. 6 is an electron microscopic image of a cross section of a titanium sintered body of Comparative Example 2.
FIG. 7 is an electron microscopic image of a cross section of a titanium ingot material of Reference Example 1.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0022] Hereinafter, a titanium sintered body and an ornament according to the invention will be described in detail with reference to preferred embodiments shown in the accompanying drawings.

Titanium Sintered Body

[0023] First, an embodiment of the titanium sintered body according to the invention will be described.

[0024] FIG. 1 is an electron microscopic image showing an embodiment of the titanium sintered body according to the invention, and FIG. 2 is a view schematically drawing a part of the electron microscopic image shown in FIG. 1. Incidentally, FIG. 1 is obtained by taking an image of a cut surface of the titanium sintered body, and a dark-colored band extending to the right and left in the upper end of FIG. 1 is a region outside the titanium sintered body.

[0025] The titanium sintered body according to this embodiment is produced by, for example, a powder metallurgy method. That is, this titanium sintered body is formed by sintering titanium alloy powder particles to one another.

[0026] More specifically, as shown in FIG. 2, a titanium sintered body 1 contains an α-phase 2 and a β-phase 3 as crystal structures. Among these, the α-phase 2 refers to a region (α-phase titanium) in which the crystal structure forming the same is mainly a hexagonal closest packed (hcp) structure. On the other hand, the β-phrase 3 refers to a region (β-phase titanium) in which the crystal structure forming the same is mainly a body-centered cubic (bcc) structure. In FIG. 1, the α-phase 2 appears as a region with a relatively light color, and the β-phase 3 appears as a region with a relatively dark color.

[0027] The α-phase 2 has relatively low hardness and high ductility, and therefore contributes to the realization of the titanium sintered body 1 having excellent strength and excellent deformation resistance particularly at a high temperature. On the other hand, the β-phase 3 has relatively high hardness, but is likely to be plastically deformed, and therefore contributes to the realization of the titanium sintered body 1 having excellent toughness as a whole.

[0028] It is preferred that most of the cross section of the titanium sintered body 1 is occupied by such an α-phase 2 and a β-phase 3. The total occupancy ratio (area ratio) of the α-phase 2 and the β-phase 3 is not particularly limited, but is preferably 95% or more, more preferably 98% or more. In such a titanium sintered body 1, the α-phase 2 and the β-phase 3 become dominant in characteristics, and therefore, the titanium sintered body 1 reflects many advantages of titanium.

[0029] The total occupancy ratio of the α-phase 2 and the β-phase 3 is obtained by, for example, observing the cross section of the titanium sintered body 1 by an electron microscope or a light microscope and distinguishing the crystal phases based on the difference in color or the contrast due to the difference in crystal structure and also measuring the areas.

[0030] Examples of crystal structures other than the α-phase 2 and the β-phase 3 include a ω-phase and a γ-phase.

[0031] The titanium sintered body 1 contains the α-phase 2 and the β-phase 3 as described above, and also the average grain size of the α-phase 2 is 3 μm or more and 30 μm or less, and the occupancy ratio (area ratio) of the α-phase 2 is 70% or more and 99.8% or less.

[0032] In such a titanium sintered body 1, since the α-phase 2 is minute and also the α-phase 2 is dominant, the strength is high and also the uniformity of polishing processing is high. Due to this, when polishing processing is performed for the titanium sintered body 1, unevenness caused by a difference in the hardness between the α-phase 2 and the β-phase 3 is less likely to occur, and thus, the smoothness of the polished surface can be increased. In addition, the α-phase 2 which is dominantly present hardly causes translocation and therefore is hardly denatured by polishing and also has high corrosion resistance, and thus contributes to the maintenance of a smooth state immediately after polishing for a long period of time. In other words, the wear resistance is high, and therefore, scratching or the like of the polished surface is suppressed, so that the polished surface can be kept good for a long period of time. On the other hand, the β-phase 3 whose amount of presence is smaller than that of the α-phase 2 is likely to be plastically deformed as described above, and therefore promotes the mutual sliding of the grains of the α-phase 2. Due to this, even if stress is applied during polishing processing, the stress can be alleviated in the β-phase 3. As a result, a problem such as a decrease in smoothness due to residual stress can be prevented from occurring. In other words, a polishing property enabling favorable polishing is obtained, and therefore, a polished surface having high specularity can be easily obtained.

[0033] When the average grain size of the α-phase 2 is less than the above lower limit, the grain size of the α-phase 2 is too small, and therefore, it is difficult to achieve appropriate polishing, and also the α-phase 2 having a small grain size is likely to affect the reflection of light, and thus, the specularity of the polished surface may be decreased. In addition, the occupancy ratio of the α-phase 2 cannot be sufficiently increased, and therefore, the mechanical strength of the titanium sintered body 1 may not be able to be sufficiently increased. On the other hand, when the average grain size of the α-phase 2 exceeds the above upper limit, the α-phase 2 is likely to have a needle shape. When the α-phase 2 has a needle shape, the fatigue strength of the titanium sintered body 1 is easy to decrease, and therefore, it becomes difficult to maintain high specularity for a long period of time. Further, the wear resistance is decreased, and therefore, the polished surface is likely to be scratched, and it may be difficult to keep the polished surface good for a long period of time. In addition, the mechanical strength attributed mainly to the α-phase 2 may be decreased.

[0034] When the area ratio occupied by the α-phase 2 is lower than the above lower limit, the area occupied by the β-phase 3 is increased by that amount. Due to this, the degree of contribution to the reflection of light by the β-phase 3 is increased, and thus, the specularity of the polished surface is decreased. On the other hand, when the area ratio occupied by the α-phase 2 exceeds the above upper limit, the amount of presence of the β-phase 3 is decreased by that amount. Due to this, the function of the β-phase 3 of alleviating the stress generated between the grains of the α-phase 2 is deteriorated, and therefore, the smoothness of the polished surface may be decreased due to residual stress.

[0035] The average grain size of the α-phase 2 is preferably 5 μm or more and 25 μm or less, more preferably 7 μm or more and 20 μm or less.

[0036] The average grain size of the α-phase 2 is measured as follows. First, the cross section of the titanium sintered body 1 is observed by an electron microscope, and 100 or more grains of the α-phase 2 in the obtained observation image are randomly selected. Subsequently, the area of each grain of the α-phase 2 selected in the observation image is calculated, and the diameter of a circle having the same area as that of this area is obtained. The diameter of the circle obtained in this manner is regarded as the grain size (equivalent circle diameter) of the grain of the α-phase 2, and an average for 100 or more grains of the α-phase 2 is obtained. This average is determined as the average grain size of the α-phase 2.

[0037] The area ratio occupied by the α-phase 2 is preferably 75% or more and 99% or less, more preferably 80% or more and 98% or less.

[0038] The area ratio occupied by the α-phase 2 is measured as follows. First, the cross section of the titanium sintered body 1 is observed by an electron microscope, and the area of the obtained observation image is calculated. Subsequently, the total area of the α-phase 2 in the observation image is obtained. Then, the obtained total area of the α-phase 2 is divided by the area of the observation image. The solution is the area ratio occupied by the α-phase 2.

[0039] On the other hand, in the case where the α-phase 2 is present at an area ratio as described above, the area ratio of the β-phase 3 is smaller than that. Specifically, the area ratio of the β-phase 3 is preferably about 0.2% or more and 30% or less, more preferably about 1% or more and 25% or less, further more preferably about 2% or more and 20% or less. The β-phase 3 is likely to be plastically deformed as described above, and therefore promotes the mutual sliding of the grains of the α-phase 2. Due to this, in the case where the β-phase 3 is present at a ratio within the above range, when the titanium sintered body 1 is polished, the resistance during polishing can be prevented from significantly increasing. As a result, the smoothness of the polished surface can be further increased, and thus, the titanium sintered body 1 having high specularity and excellent aesthetic appearance can be obtained.

[0040] The constituent material of such a titanium sintered body 1 is a titanium simple substance or a titanium-based alloy.

[0041] The titanium-based alloy is an alloy containing titanium as a main component, but is an alloy containing, other than titanium (Ti), an element such as carbon (C), nitrogen (N), oxygen (O), aluminum (Al), vanadium (V), niobium (Nb), zirconium (Zr), tantalum (Ta), molybdenum (Mo), chromium (Cr), manganese (Mn), cobalt (Co), iron (Fe), silicon (Si), gallium (Ga), tin (Sn), barium (Ba), nickel (Ni), or sulfur (S).

[0042] Among these, the titanium-based alloy according to this embodiment preferably contains an α-phase stabilizing element and a β-phase stabilizing element. According to this, even if the production conditions or use conditions for the titanium sintered body 1 change, since the titanium sintered body 1 can have both α-phase 2 and β-phase 3 as the crystal structures, the titanium sintered body 1 has excellent weather resistance. Due to this, the titanium sintered body 1 has both characteristics exhibited by the α-phase 2 and characteristics exhibited by the β-phase 3 , and thus has particularly excellent mechanical properties.

[0043] Examples of the α-phase stabilizing element include aluminum, gallium, tin, carbon, nitrogen, and oxygen, and these are used alone or two or more types thereof are used in combination. On the other hand, examples of the β-phase stabilizing element include molybdenum, niobium, tantalum, vanadium, and iron, and these are used alone or two or more types thereof are used in combination.

[0044] As a specific composition of the titanium-based alloy, a titanium alloy specified in JIS H 4600:2012 as type 60, type 60E, type 61, or type 61F can be used. Specific examples thereof include Ti-6Al-4V, Ti-6Al-4V ELI, and Ti-3Al-2.5V. Other examples thereof include Ti-6Al-6V-2Sn, Ti-6Al-2Sn-4Zr-2Mo-0.08Si, and Ti-6Al-2Sn-4Zr-6Mo specified in Aerospace Material Specifications (AMS). Further, additional examples thereof include Ti-5Al-2.5Fe and Ti-6Al-7Nb specified in the specification made by International Organization for Standardization (ISO), and also include Ti-13Zr-13Ta, Ti-6Al-2Nb-1Ta, Ti-15Zr-4Nb-4Ta, and Ti-5Al-3Mo-4Zr.

[0045] In the notation of the above-mentioned alloy composition, the components are shown in decreasing order of concentration from left to right, and the number shown before the element indicates the concentration of the element inmass%. For example, Ti-6Al-4V shows that the alloy contains Al at 6 mass% and V at 4 mass% with the remainder consisting of Ti and impurities. The impurities are elements which are inevitably contained or elements which are added intentionally at a predetermined ratio (for example, the total amount of the impurities is 0.40 mass% or less).

[0046] Further, the ranges for main alloy compositions described above are as follows.

[0047] The Ti-6Al-4V alloy contains Al at 5. 5 mass% or more and 6.75 mass% or less and V at 3.5 mass% or more and 4.5 mass% or less with the remainder consisting of Ti and impurities. As the impurities, for example, Fe at 0.4 mass% or less, O at 0.2 mass% or less, N at 0.05 mass% or less, H at 0.015 mass% or less, and C at 0.08 mass% or less are permitted to be contained, respectively. Further, other elements are permitted to be contained at 0.10 mass% or less independently and 0.40 mass% or less in total, respectively.

[0048] The Ti-6Al-4V ELI alloy contains Al at 5.5 mass% or more and 6.5 mass% or less and V at 3.5 mass% or more and 4.5 mass% or less with the remainder consisting of Ti and impurities. As the impurities, for example, Fe at 0.25 mass% or less, O at 0.13 mass% or less, N at 0.03 mass% or less, H at 0.0125 mass% or less, and C at 0.08 mass% or less are permitted to be contained, respectively. Further, other elements are permitted to be contained at 0.10 mass% or less independently and 0.40 mass% or less in total, respectively.

[0049] The Ti-3Al-2.5V alloy contains Al at 2.5 mass% or more and 3.5 mass% or less, V at 1. 6 mass% or more and 3.4 mass% or less, S (according to need) at 0.05 mass% or more and 0.20 mass% or less, and at least one element (according to need) selected from La, Ce, Pr, and Nd at 0. 05 mass% or more and 0.70 mass% or less in total with the remainder consisting of Ti and impurities. As the impurities, for example, Fe at 0.30 mass% or less, O at 0.25 mass% or less, N at 0.05 mass% or less, H at 0.015 mass% or less, and C at 0.10 mass% or less are permitted to be contained, respectively. Further, other elements are permitted to be contained at 0.40 mass% or less in total.

[0050] The Ti-5Al-2.5Fe alloy contains Al at 4.5 mass% or more and 5.5 mass% or less and Fe at 2 mass% or more and 3 mass% or less with the remainder consisting of Ti and impurities. As the impurities, for example, O at 0.2 mass% or less, N at 0.05 mass% or less, H at 0.013 mass% or less, and C at 0.08 mass% or less are permitted to be contained, respectively. Further, other elements are permitted to be contained at 0.40 mass% or less in total.

[0051] The Ti-6Al-7Nb alloy contains Al at 5.5 mass% or more and 6.5 mass% or less and Nb at 6.5 mass% or more and 7.5 mass% or less with the remainder consisting of Ti and impurities. As the impurities, for example, Ta at 0.50 mass% or less, Fe at 0.25 mass% or less, O at 0.20 mass% or less, N at 0.05 mass% or less, H at 0.009 mass% or less, and C at 0.08 mass% or less are permitted to be contained, respectively. Further, other elements are permitted to be contained at 0.40 mass% or less in total. The Ti-6Al-7Nb alloy has particularly low cytotoxicity as compared with other alloy types, and therefore is particularly useful when the titanium sintered body 1 is used for biocompatible purposes.

[0052] The components contained in the titanium sintered body 1 can be analyzed by, for example, a method in accordance with Titanium - ICP atomic emission spectrometry specified in JIS H 1632-1 (2014) to JIS H 1632-3 (2014).

[0053] The titanium sintered body 1 may also contain particles containing titanium oxide as a main component (hereinafter simply referred to as "titanium oxide particles"). It is considered that the titanium oxide particles share the stress applied to titanium metal serving as the matrix by being dispersed in the titanium sintered body 1. Due to this, by including the titanium oxide particles, the mechanical strength of the entire titanium sintered body 1 is improved. Further, since titanium oxide is harder than titanium metal, by dispersing the titanium oxide particles, the wear resistance of the titanium sintered body 1 can be further increased. Due to this, scratching or the like of the polished surface is suppressed, and therefore, the polished surface can be kept good for a long period of time.

[0054] The "particles containing titanium oxide as a main component" refers to, for example, particles analyzed such that an element contained in the largest amount is either one of titanium and oxygen, and an element contained in the second largest is the other when a component analysis of the particles of interest is performed by an X-ray fluorescence analysis or an electron microprobe analyzer.

[0055] The average particle diameter of the titanium oxide particles is not particularly limited, but is preferably 0.5 μm or more and 20 μm or less, more preferably 1 μm or more and 15 μm or less, further more preferably 2 μm or more and 10 μm or less. When the average particle diameter of the titanium oxide particles is within the above range, the wear resistance can be increased without largely deteriorating the mechanical properties such as toughness and tensile strength of the titanium sintered body 1. That is, when the average particle diameter of the titanium oxide particles is less than the above lower limit, the effect of sharing the stress of the titanium oxide particles may be decreased depending on the content of the titanium oxide particles. Further, when the average particle diameter of the titanium oxide particles exceeds the above upper limit, the titanium oxide particle may serve as a starting point of a crack to decrease the mechanical strength depending on the content of the titanium oxide particles.

[0056] The crystal structure of the titanium oxide particle may be any of a rutile type, an anatase type, and a brookite type, and may be a mixture of a plurality of types.

[0057] The average particle diameter of the titanium oxide particles is measured as follows. First, the cross section of the titanium sintered body 1 is observed by an electron microscope, and 100 or more titanium oxide particles in the obtained observation image are randomly selected. At this time, whether a particle is the titanium oxide particle or not can be specified by the contrast of the image and an area analysis of oxygen or the like. Subsequently, the area of each titanium oxide particle selected in the observation image is calculated, and the diameter of a circle having the same area as that of this area is obtained. The diameter of the circle obtained in this manner is regarded as the particle diameter (equivalent circle diameter) of the titanium oxide particle, and an average for 100 or more titanium oxide particles is obtained. This average is determined as the average particle diameter of the titanium oxide particles.

[0058] The shape of the α-phase 2 according to this embodiment is preferably not a needle shape, but an isotropic shape or a shape equivalent thereto. When the α-phase 2 has such a shape, the decrease in the fatigue strength of the titanium sintered body 1 can be suppressed as described above. As a result, the titanium sintered body 1 capable of maintaining high specularity for a long period of time is obtained.

[0059] Specifically, in the cross section of the titanium sintered body 1, the average aspect ratio of the α-phase 2 is preferably 1 or more and 3 or less, more preferably 1 or more and 2.5 or less. When the average aspect ratio of the α-phase 2 is within the above range, the decrease in the fatigue strength and the hardness of the titanium sintered body 1 is suppressed. Due to this, the titanium sintered body 1 which is useful as a structural component is obtained. Further, by adjusting the average aspect ratio within the above range, anisotropy is less likely to occur in a polishing amount when polishing processing is performed for the titanium sintered body 1, and therefore, unevenness is less likely to occur on the polished surface. As a result, the smoothness of the polished surface can be further increased, and thus, the titanium sintered body 1 having particularly excellent specularity is obtained. In other words, when anisotropy is likely to occur in a polishing amount, anisotropy also occurs in light reflection, and thus, the specularity or the aesthetic properties may be decreased.

[0060] The average aspect ratio of the α-phase 2 is measured as follows. First, the cross section of the titanium sintered body 1 is observed by an electron microscope, and 100 or more grains of the α-phase 2 in the obtained observation image are randomly selected. Subsequently, the major axis of the grain of the α-phase 2 selected in the observation image is specified, and further, the longest axis in the direction orthogonal to this major axis is specified as the minor axis. Then, the ratio of the major axis to the minor axis is calculated as the aspect ratio. Then, the aspect ratios of 100 or more grains of the α-phase 2 is averaged, and the resulting value is determined as the average aspect ratio.

[0061] In the titanium sintered body 1 according to this embodiment, the α-phase 2 has a relatively uniform grain size. Due to this, not only because of having an isotropic shape or a shape equivalent thereto, but also having a uniform grain size, the fatigue strength of the titanium sintered body 1 is increased, and also the specularity can be kept high for a long period of time.

[0062] When the measurement result of the grain size of the α-phase 2 is plotted in a plot area in which the horizontal axis represents the grain size of the α-phase 2 and the vertical axis represents the number of grains of the α-phase 2 corresponding to the grain size, a grain size distribution of the α-phase 2 is obtained. In this grain size distribution, the grain size when the cumulative number of grains from the small grain size side reaches 16% of the total is represented by D16, and the grain size when the cumulative number of grains from the small grain size side reaches 84% of the total is represented by D84. At this time, the standard deviation SD of the grain size distribution is obtained according to the following formula.

following formula.

$$SD = (D84-D16)/2$$

[0063] The standard deviation SD obtained in this manner serves as the index of the distribution width of the grain size distribution. In the titanium sintered body 1 according to this embodiment, the standard deviation SD of the grain size distribution of the α-phase 2 is preferably 5 or less, more preferably 3 or less, further more preferably 2 or less. In the titanium sintered body 1 in which the standard deviation SD of the grain size distribution of the α-phase 2 is within the above range, the grain size distribution is sufficiently narrow, and also the grain size of the α-phase 2 is sufficiently uniform. Such a titanium sintered body 1 has particularly high fatigue strength, and can maintain high specularity for a long period of time.

[0064] Further, an X-ray diffraction spectrum obtained by subjecting the titanium sintered body 1 to a crystal structure analysis by X-ray diffractometry includes a peak reflection intensity derived from the α-phase and a peak reflection intensity derived from the β-phase.

[0065] Here, it is preferred that the obtained X-ray diffraction spectrum particularly includes a peak reflection intensity by the plane orientation (100) of the α-phase titanium and a peak reflection intensity by the plane orientation (110) of the β-phase titanium. In addition, the value of the peak reflection intensity (the value of the peak top) by the plane orientation (110) of the β-phase titanium is preferably 3% or more and 60% or less, more preferably 5% or more and 50% or less, further more preferably 10% or more and 40% or less of the value of the peak reflection intensity (the value of the peak top) by the plane orientation (100) of the α-phase titanium. According to this, both characteristics of the α-phase 2 and characteristics of the β-phase 3 described above become obvious without being buried. As a result, the titanium sintered body 1 capable of maintaining high specularity particularly for a long period of time is obtained.

[0066] The peak reflection intensity by the plane orientation (100) of the α-phase titanium is located at 2θ of about 35.3°. On the other hand, the peak reflection intensity by the plane orientation (110) of the β-phase titanium is located at 2θ of about 39.5°.

[0067] As the X-ray source of the X-ray diffractometer, Cu-Kα radiation is used, and the tube voltage is set to 30 kV, and the tube current is set to 20 mA.

[0068] Further, the titanium sintered body 1 has a relative density of preferably 99% or more, more preferably 99.5% or more. By setting the relative density of the titanium sintered body 1 within the above range, the titanium sintered body 1 having particularly good specularity when polishing the surface is obtained. That is, when the titanium sintered body 1 has a relative density within the above range, pores are hardly formed in the titanium sintered body 1. Due to this, the inhibition of light reflection by such pores can be suppressed.

[0069] The relative density of the titanium sintered body 1 is a dry density measured in accordance with the test method of density of sintered metal materials specified in JIS Z 2501:2000.

[0070] Further, the Vickers hardness (HV) of the titanium sintered body 1 is not particularly limited, but is preferably 300 or more, more preferably 350 or more and 600 or less. The titanium sintered body 1 having such a hardness is less likely to be scratched or the like on the surface. Due to this, the titanium sintered body 1 capable of suppressing the deterioration of the sense of beauty by a scratch or the like even if the titanium sintered body 1 is used as a constituent material of, for example, an ornament or the like is obtained.

[0071] The Vickers hardness (HV) of the titanium sintered body 1 is measured on the surface of the titanium sintered body 1, and the measurement method is in accordance with Vickers hardness test - Test method specified in JIS Z 2244:2009. Incidentally, a test force applied by an indenter is set to 9.8 N (1 kgf), and a test force duration is set to 15 seconds. Then, an average of the measurement results at 10 sites is determined as the surface Vickers hardness.

[0072] Such a titanium sintered body 1 can be applied to various uses and is particularly useful as a constituent material of an ornament, although the use thereof is not particularly limited.

Ornament

[0073] Next, an embodiment of an ornament according to the invention will be described.

[0074] Examples of the ornament according to the invention include external components for watches such as watch cases (case bodies, case backs, one-piece cases in which a case body and a case back are integrated, etc.), watch bands (including band clasps, band-bangle attachment mechanisms, etc.), bezels (for example, rotatable bezels, etc.), crowns (for example, screw-lock crowns, etc.), buttons, glass frames, dial rings, etching plates, and packings, personal ornaments such as glasses (for example, glasses frames), tie clips, cuff buttons, rings, necklaces, bracelets, anklets, brooches, pendants, earrings, and pierced earrings, utensils such as spoons, forks, chopsticks, knives, butter knives, and corkscrews, lighters or lighter cases, sports goods such as golf clubs, nameplates, panels, prize cups, and external components for apparatuses such as housings (for example, housings for cellular phones, smartphones, tablet terminals, mobile computers, music players, cameras, shavers, etc.). For any of these ornaments, excellent aesthetic appearance is sometimes considered important. By using the titanium sintered body 1 as a constituent material of these ornaments, excellent specularity can be imparted to the surface of the ornaments. According to this, ornaments capable of maintaining excellent aesthetic appearance for a long period of time is obtained.

[0075] FIG. 3 is a perspective view showing a watch case to which the embodiment of the ornament according to the invention is applied. FIG. 4 is a partial cross-sectional perspective view showing a bezel to which the embodiment of the ornament according to the invention is applied.

[0076] A watch case 11 shown in FIG. 3 includes a case main body 112 and a band attachment section 114 for attaching a watch band provided protruding from the case main body 112. Such a watch case 11 can form a container along with a glass plate (not shown) and a case back (not shown). In this container, a movement (not shown), a dial plate (not shown), etc. are housed. Therefore, this container protects the movement and the like from the external environment and also has a large influence on the aesthetic appearance of the watch.

[0077] A bezel 12 shown in FIG. 4 has an annular shape, and is attached to a watch case, and is rotatable with respect to the watch case as needed. When the bezel 12 is attached to a watch case, the bezel 12 is located outside the watch case, and therefore has an influence on the aesthetic appearance of the watch.

[0078] Further, such a watch case 11 and a bezel 12 are used in a state where they are attached to the human body, and therefore are likely to be scratched at all times. Due to this, by using the titanium sintered body 1 as a constituent material of such an ornament, an ornament having high specularity on the surface and also having excellent aesthetic appearance is obtained. In addition, this specularity can be maintained for a long period of time.

Method for Producing Titanium Sintered Body

[0079] Next, a method for producing the titanium sintered body 1 will be described.

[0080] The method for producing the titanium sintered body 1 includes [1] a step of obtaining a kneaded material by kneading a titanium alloy powder and an organic binder, [2] a step of obtaining a molded body by molding the kneaded material by a powder metallurgy method, [3] a step of obtaining a degreased body by degreasing the molded body, [4] a step of obtaining a sintered body by firing the degreased body, and [5] a step of performing a hot isostatic pressing treatment (HIP treatment) for the sintered body. Hereinafter, the respective steps will be sequentially described.

[1] Kneading Step

[0081] First, a titanium simple substance powder or a titanium alloy powder (hereinafter simply referred to as "titanium alloy powder") to serve as a starting material of the titanium sintered body 1 is kneaded along with an organic binder, whereby a kneaded material is obtained.

[0082] The average particle diameter of the titanium alloy powder is not particularly limited, but is preferably 1 μm or more and 50 μm or less, more preferably 5 μm or more and 40 μm or less.

[0083] The titanium alloy powder may be a powder (a pre-alloy powder) composed only of particles having a single alloy composition or may be a mixed powder (a pre-mix powder) obtained by mixing a plurality of types of particles having different compositions from one another. In the case of a pre-mix powder, an individual particle may be a particle containing only one type of element or a particle containing a plurality of elements as long as a compositional ratio as described above is satisfied as a whole pre-mix powder.

[0084] The content of the organic binder in the kneaded material is appropriately set according to the molding conditions, the shape to be molded, or the like, but is preferably about 2 mass% or more and 20 mass% or less, more preferably about 5 mass% or more and 10 mass% or less of the total amount of the kneaded material. By setting the content of the organic binder within the above range, the kneaded material has favorable fluidity. According to this, the filling property of the kneaded material when performing molding is improved, and a sintered body having a shape closer to a final desired shape (near-net shape) is obtained.

[0085] Examples of the organic binder include polyolefins such as polyethylene, polypropylene, and ethylene-vinyl acetate copolymers, acrylic resins such as polymethyl methacrylate and polybutyl methacrylate, styrenic resins such as polystyrene, polyesters such as polyvinyl chloride, polyvinylidene chloride, polyamide, polyethylene terephthalate, and polybutylene terephthalate, various resins such as polyether, polyvinyl alcohol, polyvinylpyrrolidone, and copolymers thereof, and various organic binders such as various waxes, paraffins, higher fatty acids (such as stearic acid), higher alcohols, higher fatty acid esters, and higher fatty acid amides. These can be used alone or by mixing two or more types thereof.

[0086] In the kneaded material, a plasticizer may be added as needed. Examples of the plasticizer include phthalate esters (such as DOP, DEP, and DBP), adipate esters, trimellitate esters, and sebacate esters. These can be used alone or by mixing two or more types thereof.

[0087] Further, in the kneaded material, other than the titanium alloy powder, the organic binder, and the plasticizer, for example, any of a variety of additives such as a lubricant, an antioxidant, a degreasing accelerator, and a surfactant can be added as needed.

[0088] The kneading conditions vary depending on the respective conditions such as the alloy composition or the particle diameter of the titanium alloy powder to be used, the composition of the organic binder, and the blending amount thereof. However, for example, the kneading temperature can be set to about 50°C or higher and 200°C or lower, and the kneading time can be set to about 15 minutes or more and 210 minutes or less.

[0089] Further, the kneaded material is formed into a pellet (small particle) as needed. The particle diameter of the pellet is set to, for example, about 1 mm or more and 15 mm or less.

[0090] Incidentally, depending on the molding method described below, in place of the kneaded material, a granulated powder may be produced.

[2] Molding Step

[0091] Subsequently, the kneaded material is molded, whereby a molded body is produced.

[0092] The molding method is not particularly limited, and for example, any of a variety of molding methods such as a powder compacting (compression molding) method, a metal injection molding (MIM) method, and an extrusion molding method can be used. Among these, from the viewpoint that a sintered body having a near-net shape can be produced, a metal injection molding method is preferably used.

[0093] The molding conditions in the case of a powder compacting method are preferably such that the molding pressure is about 200 MPa or more and 1000 MPa or less (2 t/cm^2 or more and 10 t/cm^2 or less), which vary depending on the respective conditions such as the composition and the particle diameter of the titanium alloy powder to be used, the composition of the organic binder, and the blending amount thereof.

[0094] The molding conditions in the case of the titanium alloy powder are preferably such that the material temperature is about 80°C or higher and 210°C or lower, and the injection pressure is about 50 MPa or more and 500 MPa or less (0.5 t/cm^2 or more and 5 t/cm^2 or less), which also vary depending on the respective conditions.

[0095] The molding conditions in the case of an extrusion molding method are preferably such that the material temperature is about 80°C or higher and 210°C or lower, and the extrusion pressure is about 50 MPa or more and 500 MPa or less (0.5 t/cm^2 or more and 5 t/cm^2 or less), which also vary depending on the respective conditions.

[0096] The thus obtained molded body is in a state where the organic binder is uniformly distributed in gaps between the particles of the titanium alloy powder.

[0097] The shape and size of the molded body to be produced are determined in anticipation of shrinkage of the molded body in the subsequent degreasing step and firing step.

[0098] Further, according to need, the molded body may be subj ected to machining processing such as grinding, polishing, or cutting. The molded body has a relatively low hardness and relatively high plasticity, and therefore, the machining processing can be easily performed while preventing the molded body from losing its shape. According to such machining processing, the titanium sintered body 1 having high dimensional accuracy can be more easily obtained in the end.

[3] Degreasing Step

[0099] Subsequently, the thus obtained molded body is subjected to a degreasing treatment (binder removal treatment), whereby a degreased body is obtained.

[0100] Specifically, the degreasing treatment is performed in such a manner that the organic binder is decomposed by heating the molded body, whereby at least part of the organic binder is removed from the molded body.

[0101] Examples of the degreasing treatment include a method of heating the molded body and a method of exposing the molded body to a gas capable of decomposing the binder.

[0102] In the case of using a method of heating the molded body, the conditions for heating the molded body are preferably such that the temperature is about 100°C or higher and 750°C or lower and the time is about 0.1 hours or more and 20 hours or less, and more preferably such that the temperature is about 150°C or higher and 600°C or lower and the time is about 0.5 hours or more and 15 hours or less, which slightly vary depending on the composition and the blending amount of the organic binder. According to this, the degreasing of the molded body can be necessarily and sufficiently performed without sintering the molded body. As a result, it is possible to reliably prevent the organic binder component from remaining inside the degreased body in a large amount.

[0103] The atmosphere when the molded body is heated is not particularly limited, and an atmosphere of a reducing gas such as hydrogen, an atmosphere of an inert gas such as nitrogen or argon, an atmosphere of an oxidative gas such as air, a reduced pressure atmosphere obtained by reducing the pressure of such an atmosphere, or the like can be used.

[0104] Examples of the gas capable of decomposing the binder include ozone gas.

[0105] Incidentally, by dividing this degreasing step into a plurality of steps in which the degreasing conditions are different, and performing the plurality of steps, the organic binder in the molded body can be more rapidly decomposed and removed so that the organic binder does not remain in the molded body.

[0106] Further, according to need, the degreased body may be subjected to machining processing such as grinding, polishing, or cutting. The degreased body has a relatively low hardness and relatively high plasticity, and therefore, the machining processing can be easily performed while preventing the degreased body from losing its shape. According to such machining processing, the titanium sintered body 1 having high dimensional accuracy can be more easily obtained in the end.

(4) Firing Step

[0107] Subsequently, the obtained degreased body is fired in a firing furnace, whereby a sintered body is obtained. That is, diffusion occurs at the boundary surface between the particles of the titanium alloy powder, resulting in sintering. As a result, the titanium sintered body 1 is obtained.

[0108] The firing temperature varies depending on the composition, the particle diameter, and the like of the titanium alloy powder, but is set to, for example, about 900°C or higher and 1400°C or lower, and preferably set to about 1050°C or higher and 1300°C or lower.

[0109] The firing time is set to 0.2 hours or more and 20 hours or less, but is preferably set to about 1 hour or more and 6 hours or less.

[0110] In the firing step, the firing temperature or the below-described firing atmosphere may be changed in the middle of the step.

[0111] The atmosphere when performing firing is not particularly limited, however, in consideration of prevention of significant oxidation of the metal powder, an atmosphere of a reducing gas such as hydrogen, an atmosphere of an inert gas such as argon, a reduced pressure atmosphere obtained by reducing the pressure of such an atmosphere, or the like is preferably used.

[0112] In the case where the titanium sintered body 1 is produced from the titanium alloy powder, depending on the firing conditions or the like, both α-phase 2 and β-phase 3 are sometimes formed. In particular, in the case where the above-mentioned β-phase stabilizing element is contained in the titanium alloy powder, the β-phase 3 is more reliably formed.

[0113] On the other hand, by optimizing the respective production conditions, the ratio occupied by the α-phase 2 in the titanium sintered body 1, that is, the area ratio occupied by the α-phase 2 in the cross section of the titanium sintered body 1 can be adjusted. For example, when the firing temperature is increased, the ratio of the β-phase 3 is increased, and therefore, the firing temperature may be adjusted so that the ratio of the β-phase 3 falls within the desired range, and also the firing time may be set in consideration of the increase in the size of the crystal structure caused by a too long firing time.

[0114] Therefore, for example, in the case where the titanium sintered body 1 is produced using the titanium alloy powder which contains almost no β-phase 3, depending on the composition of the titanium alloy powder, the ratio of the β-phase 3 is increased as the firing temperature is increased, and therefore, the firing temperature is adjusted so that the area ratio of the α-phase 2 falls within the above range, and also the firing time is set so that insufficient sintering or excessive sintering is not caused by adjusting the firing temperature.

[0115] Further, in the case where the average grain size of the α-phase 2 is within the above range, as the area ratio of the α-phase 2 is increased, the shape of the α-phase 2 tends to be close to an isotropic shape. This is considered to be because the probability that the grains of the α-phase 2 are located adjacent to each other is increased as the ratio of the β-phase 3 is decreased, and anisotropic grain growth is inhibited by the grains of the α-phase 2 interfering with each other.

[5] HIP Step

[0116] The thus obtained sintered body may be further subjected to an HIP treatment (hot isostatic pressing treatment) or the like. By doing this, the density of the sintered body is further increased, and thus, an ornament having further excellent mechanical properties can be obtained.

[0117] As the conditions for the HIP treatment, for example, the temperature is set to 850°C or higher and 1200°C or lower, and the time is set to about 1 hour or more and 10 hours or less.

[0118] Further, the pressure to be applied is preferably 50 MPa or more, more preferably 100 MPa or more and 500 MPa or less.

[0119] In addition, the obtained sintered body may be further subjected to an annealing treatment, a solution heat treatment, an aging treatment, a hot working treatment, a cold working treatment, or the like as needed.

[0120] The obtained titanium sintered body 1 may be subjected to a polishing treatment as needed. The polishing treatment is not particularly limited, however, examples thereof include electrolytic polishing, buffing, dry polishing, chemical polishing, barrel polishing, and sand blasting. By performing such a polishing treatment, metallic luster is further given to the surface of the titanium sintered body 1, and the specularity can be increased.

[0121] Hereinabove, the titanium sintered body and the ornament according to the invention have been described with reference to preferred embodiments, however, the invention is not limited thereto.

[0122] For example, the use of the titanium sintered body is not limited to the ornament, and may be various structural components and the like. Examples of the structural components include components for transport machinery such as components for automobiles, components for bicycles, components for railroad cars, components for ships, components for airplanes, and components for space transport machinery (such as rockets), components for electronic devices such as components for personal computers and components for cellular phone terminals, components for electrical devices such as refrigerators, washing machines, and cooling and heating machines, components for machines such as machine tools and semiconductor production devices, components for plants such as atomic power plants, thermal power plants, hydroelectric power plants, oil refinery plants, and chemical complexes, medical devices such as surgical instruments, artificial bones, joint prostheses, artificial teeth, artificial dental roots, and orthodontic components.

[0123] The titanium sintered body has high biocompatibility, and therefore is particularly useful as an artificial bone and a dental metal component. Among these, the dental metal component is not particularly limited as long as it is a metal component which is temporarily or semipermanently retained in the mouth, and examples thereof include metal frames such as an inlay, a crown, a bridge, a metal base, a denture, an implant, an abutment, a fixture, and a screw.

Examples

[0124] Next, specific examples of the invention will be described.

1. Production of Titanium Sintered Body

Example 1

[0125]

(1) First, a Ti-6Al-4V alloy powder having an average particle diameter of 23 μm produced by gas atomization method was prepared.
Subsequently, a mixture (organic binder) of polypropylene and a wax was prepared and weighed so that the mass ratio of the starting material powder to the organic binder was 9:1, whereby a composition for producing a titanium sintered body was obtained.
Subsequently, the obtained composition for producing a titanium sintered body was kneaded using a kneader, whereby a compound was obtained. Then, the compound was processed into pellets.
(2) Subsequently, molding was performed under the following molding conditions using the obtained pellets, whereby a molded body was produced.
Molding Conditions

- Molding method: metal injection molding method
- Material temperature: 150°C
- Injection pressure: 11 MPa (110 kgf/cm^2)

(3) Subsequently, the obtained molded body was subjected to a degreasing treatment under the following degreasing conditions, whereby a degreased body was obtained.
Degreasing Conditions

- Degreasing temperature: 520°C
- Degreasing time: 5 hours
- Degreasing atmosphere: nitrogen gas atmosphere

(4) Subsequently, the obtained degreased body was fired under the following firing conditions, whereby a sintered body was produced.
Firing Conditions

- Firing temperature: 1100°C
- Firing time: 5 hours
- Firing atmosphere: argon gas atmosphere
- Pressure in atmosphere: atmospheric pressure (100 kPa)

(5) Subsequently, the obtained sintered body was subjected to an HIP treatment under the following treatment conditions, whereby a titanium sintered body having the shape of a rod with a diameter of 5 mm and a length of 100 mm was obtained.
HIP Treatment Conditions

- Treatment temperature: 900°C
- Treatment time: 3 hours
- Treatment pressure: 1480 kgf/cm^2 (145 MPa)

(6) Subsequently, the obtained titanium sintered body was cut and the cut surface was polished by a buffing treatment.

[0126] Subsequently, the polished surface was observed by an electron microscope, and the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were obtained, respectively. The results are shown in Table 1.

Examples 2 to 6

[0127] Titanium sintered bodies were obtained in the same manner as in Example 1 except that the production conditions were changed so that the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were as shown in Table 1, respectively.

Comparative Examples 1 to 3

[0128] Titanium sintered bodies were obtained in the same manner as in Example 1 except that the production conditions were changed so that the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were as shown in Table 1, respectively.

Reference Example 1

[0129] First, a Ti-6Al-4V alloy ingot material was prepared.
[0130] Subsequently, the prepared ingot material was cut and the cut surface was polished by a buffing treatment.
[0131] Subsequently, the polished surface was observed by an electron microscope, and the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were obtained, respectively. The results are shown in Table 1.

Example 7

[0132] A titanium sintered body was obtained in the same manner as in Example 1 except that a Ti-3Al-2.5V alloy powder having an average particle diameter of 23 μm was used in place of the Ti-6Al-4V alloy powder.
[0133] Then, the obtained titanium sintered body was cut and the cut surface was polished by a buffing treatment.
[0134] Subsequently, the polished surface was observed by an electron microscope, and the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were obtained, respectively. The results are shown in Table 2.

Examples 8 to 12

[0135] Titanium sintered bodies were obtained in the same manner as in Example 7 except that the production conditions were changed so that the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were as shown in Table 2, respectively.

Comparative Examples 4 to 6

[0136] Titanium sintered bodies were obtained in the same manner as in Example 7 except that the production conditions were changed so that the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were as shown in Table 2, respectively.

Reference Example 2

[0137] First, a Ti-3Al-2.5V alloy ingot material was prepared.
[0138] Subsequently, the prepared ingot material was cut and the cut surface was polished by a buffing treatment.
[0139] Subsequently, the polished surface was observed by an electron microscope, and the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were obtained, respectively. The results are shown in Table 2.

Example 13

[0140] A titanium sintered body was obtained in the same manner as in Example 1 except that a Ti-6Al-7Nb alloy powder having an average particle diameter of 25 μm was used in place of the Ti-6Al-4V alloy powder.
[0141] Then, the obtained titanium sintered body was cut and the cut surface was polished by a buffing treatment.
[0142] Subsequently, the polished surface was observed by an electron microscope, and the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were obtained, respectively. The results are shown in Table 3.

Examples 14 to 18

[0143] Titanium sintered bodies were obtained in the same manner as in Example 13 except that the production conditions were changed so that the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were as shown in Table 3, respectively.

Comparative Examples 7 to 9

[0144] Titanium sintered bodies were obtained in the same manner as in Example 13 except that the production conditions were changed so that the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were as shown in Table 3, respectively.

Reference Example 3

[0145] First, a Ti-6Al-7Nb alloy ingot material was prepared.
[0146] Subsequently, the prepared ingot material was cut and the cut surface was polished by a buffing treatment.
[0147] Subsequently, the polished surface was observed by an electron microscope, and the average grain size of the α-phase, the area ratios occupied by the α-phase and the β-phase, and the average aspect ratio of the α-phase were obtained, respectively. The results are shown in Table 3.

2. Evaluation of Titanium Sintered Body

2.1. Specularity

[0148] First, with respect to each of the titanium sintered bodies and titanium ingot materials of the respective Examples, Comparative Examples, and Reference Examples, the polished surface was visually observed. Then, the specularity of the polished surface was evaluated according to the following evaluation criteria. The evaluation results are shown in Tables 1 to 3.

Evaluation Criteria for Specularity of Polished Surface

[0149]

A: The specularity of the polished surface is very high (the aesthetic appearance is particularly good).
B: The specularity of the polished surface is slightly high (the aesthetic appearance is slightly good).
C: The specularity of the polished surface is slightly low (the aesthetic appearance is slightly poor).
D: The specularity of the polished surface is very low (the aesthetic appearance is poor).

2.2. Relative Density

[0150] Subsequently, with respect to each of the titanium sintered bodies and titanium ingot materials of the respective Examples, Comparative Examples, and Reference Examples, the relative density was calculated in accordance with the method specified in JIS Z 2501:2000. The calculation results are shown in Tables 1 to 3.

2.3. Vickers Hardness

[0151] Subsequently, with respect to the polished surface of each of the titanium sintered bodies and titanium ingot materials of the respective Examples, Comparative Examples, and Reference Examples, the Vickers hardness was measured in accordance with the method specified in JIS Z 2244:2009. The measurement results are shown in Tables 1 to 3.

2.4. Crystal Structure Analysis by X-ray Diffractometry

[0152] Subsequently, with respect to the titanium sintered body of Example 1, a crystal structure analysis was performed by X-ray diffractometry under the following measurement conditions.

Measurement Conditions for Crystal Structure Analysis by X-ray Diffractometry

[0153]

- X-ray source: Cu-Kα radiation
- Tube voltage: 30 kv
- Tube current: 20 mA

[0154] The obtained X-ray diffraction spectrum is shown in FIG. 5.
[0155] As apparent from FIG. 5, it was found that the X-ray diffraction spectrum obtained for the titanium sintered body of Example 1 includes a peak reflection intensity by the α-phase (α-Ti) and a peak reflection intensity by the β-phase (β-Ti). Then, the value of the peak reflection intensity by the α-Ti in the plane orientation (100) located at 2θ of about 35.3° was used as the standard, and the ratio (peak ratio) of the value of the peak reflection intensity by the β-Ti in the plane orientation (110) located at 2θ of about 39.5° to the standard was calculated. In addition, the same calculation was also performed for each of the titanium sintered bodies and titanium ingot materials of Examples 2 to 18, Comparative Examples 1 to 9, and Reference Examples 1 to 3. The calculation results of the peak ratio are shown in Table 1 to 3.

2.5. Wear Resistance

[0156] Subsequently, with respect to each of the titanium sintered bodies of the respective Examples and Comparative Examples and each of the titanium ingot materials and the like of the respective Reference Examples, the wear resistance of the surface thereof was evaluated. Specifically, first, the surface of each of the titanium sintered bodies and the titanium ingot materials was polished by a buffing treatment. Subsequently, for the polished surface, a wear resistance test was performed in accordance with Testing method for wear resistance of fine ceramics by ball-on-disc method specified in JIS R 1613 (2010), and a wear amount of a disk-shaped test piece was measured. The measurement conditions were as follows.

Measurement Conditions for Specific Wear Amount

[0157]

- Material of spherical test piece: high carbon chromium bearing steel (SUJ2)
- Size of spherical test piece: diameter: 6 mm
- Material of disk-shaped test piece: each of titanium sintered bodies of respective Examples and Comparative Examples and each of titanium ingot materials of respective Reference Examples
- Size of disk-shaped test piece: diameter: 35 mm, thickness: 5 mm
- Magnitude of load: 10 N
- Sliding rate: 0.1 m/s
- Sliding circle diameter: 30 mm
- Sliding distance: 50 m

[0158] Then, the wear amount obtained for the titanium ingot material of Reference Example 1 was taken as 1, and the relative value of the wear amount obtained for each of the titanium sintered bodies of the respective Examples and Comparative Examples shown in Table 1 was calculated.
[0159] Similarly, the wear amount obtained for the titanium ingot material of Reference Example 2 was taken as 1, and the relative value of the wear amount obtained for each of the titanium sintered bodies of the respective Examples and Comparative Examples shown in Table 2 was calculated.
[0160] Further similarly, the wear amount obtained for the titanium ingot material of Reference Example 3 was taken as 1, and the relative value of the wear amount obtained for each of the titanium sintered bodies of the respective Examples and Comparative Examples shown in Table 3 was calculated.
[0161] Then, the calculated relative value was evaluated according to the following evaluation criteria. The evaluation results are shown in Tables 1 to 3.

Evaluation Criteria for Wear Amount

[0162]

A: The wear amount is very small (the relative value is less than 0.5).
B: The wear amount is small (the relative value is 0.5 or more and less than 0.75).
C: The wear amount is slightly small (the relative value is 0.75 or more and less than 1).
D: The wear amount is slightly large (the relative value is 1 or more and less than 1.25).
E: The wear amount is large (the relative value is 1.25 or more and less than 1.5).
F: The wear amount is very large (the relative value is more than 1.5).

2.6. Tensile Strength

[0163] Subsequently, with respect to each of the titanium sintered bodies of the respective Examples and Comparative Examples and each of the titanium ingot materials and the like of the respective Reference Examples, the tensile strength was measured. The measurement of the tensile strength was performed in accordance with the metal material tensile test method specified in JIS Z 2241 (2011).
[0164] Then, the tensile strength obtained for the titanium ingot material of Reference Example 1 was taken as 1, and the relative value of the tensile strength obtained for each of the titanium sintered bodies of the respective Examples and Comparative Examples shown in Table 1 was calculated.
[0165] Similarly, the tensile strength obtained for the titanium ingot material of Reference Example 2 was taken as 1, and the relative value of the tensile strength obtained for each of the titanium sintered bodies of the respective Examples and Comparative Examples shown in Table 2 was calculated.
[0166] Further similarly, the tensile strength obtained for the titanium ingot material of Reference Example 3 was taken as 1, and the relative value of the tensile strength obtained for each of the titanium sintered bodies of the respective Examples and Comparative Examples shown in Table 3 was calculated.
[0167] Then, the obtained relative value was evaluated according to the following evaluation criteria. The evaluation results are shown in Tables 1 to 3. As for the tensile strength, other than the above-mentioned test specimens, also an SUS316L sintered body, a cast material and a sintered body of ASTM F75 (a CO-28%Cr-6%Mo alloy), and an α-Ti sintered body were evaluated as Reference Examples a to d (Table 1). Further, with respect to Reference Example d, the same evaluation as in the above-mentioned 2.1. to 2.3. and 2.5. was performed in addition to 2.6.

Evaluation Criteria for Tensile Strength

[0168]

A: The tensile strength is very large (the relative value is 1.09 or more).
B: The tensile strength is large (the relative value is 1.06 or more and less than 1.09).
C: The tensile strength is slightly large (the relative value is 1.3 or more and less than 1.06).
D: The tensile strength is slightly small (the relative value is 1 or more and less than 1.03).
E: The tensile strength is small (the relative value is 0.97 or more and less than 1).
F: The tensile strength is very small (the relative value is less than 0.97).

2.7. Nominal Strain at Break (Elongation at Break)

[0169] Subsequently, with respect to each of the titanium sintered bodies of the respective Examples and Comparative

Examples and each of the titanium ingot materials and the like of the respective Reference Examples, the elongation at break was measured. The measurement of the elongation at break was performed in accordance with the metal material tensile test method specified in JIS Z 2241 (2011).

[0170] Then, the obtained elongation at break was evaluated according to the following evaluation criteria. The evaluation results are shown in Tables 1 to 3. As for the elongation at break, other than the above-mentioned test specimens, also an SUS316L sintered body, a cast material and a sintered body of ASTM F75 (a CO-28%Cr-6%Mo alloy), and an α-Ti sintered body were evaluated as Reference Examples a to d (Table 1).

Evaluation Criteria for Elongation at Break

[0171]

A: The elongation at break is very large (0.15 or more).
B: The elongation at break is large (0.125 or more and less than 0.15).
C: The elongation at break is slightly large (0.10 or more and less than 0.125).
D: The elongation at break is slightly small (0.075 or more and less than 0.10).
E: The elongation at break is small (0.050 or more and less than 0.075).
F: The elongation at break is very small (less than 0.050).

2.8. Cytotoxicity Test

[0172] Subsequently, with respect to a test specimen composed of each of the titanium sintered bodies of the respective Examples and Comparative Examples and each of the titanium ingot materials and the like of the respective Reference Examples, a cytotoxicity test was performed. The cytotoxicity test was performed in accordance with the cytotoxicity test specified in ISO 10993-5:2009. Specifically, by a colony formation method using a direct contact method, an average of the number of colonies in a control group is taken as 100%, and the ratio of the number of colonies of cells directly inoculated onto the test specimen to the number of colonies in the control group (colony formation ratio (%)) was obtained. The test conditions were as follows.

- Cell line: V97 cell line
- Culture medium: MEM10 medium
- Negative control material (negative control): high-density polyethylene film
- Positive control material (positive control) : 0.1% zinc diethyldithiocarbamate-containing polyurethane film
- Control group (control) : the number of colonies of cells directly inoculated into the culture medium

[0173] Subsequently, the obtained colony formation ratio was classified according to the following evaluation criteria, whereby the cytotoxicity of each test specimen was evaluated. The evaluation results are shown in Tables 1 to 3. As for the cytotoxicity test, other than the above-mentioned test specimens, also an SUS316L sintered body, a sintered body of ASTM F75 (a CO-28%Cr-6%Mo alloy), and an α-Ti sintered body were evaluated as Reference Examples a, c, and d (Table 1).

Evaluation Criteria for Cytotoxicity

[0174]

A: The colony formation ratio is 90% or more.
B: The colony formation ratio is 80% or more and less than 90%.
C: The colony formation ratio is less than 80%.

Table 1

		Structure of titanium sintered body							Evaluation results						
	Production method	Composition	Crystal structure	α-phase			β-phase	X-ray diffraction peak ratio	Specularity	Relative density	Vickers hardness	Wear resistance	Tensile strength	Elongation at break	Cytotoxicity test
				Average grain size	Area ratio	Aspect ratio	Area ratio								
	-	-	-	μm	%	-	%	%	-	%	-	-	-	-	-
Example 1	Sintered body	Ti-6Al-4V	α+β	15	82	1.8	18	28	A	99.8	380	A	A	B	B
Example 2	Sintered body	Ti-6Al-4V	α+β	12	88	1.6	12	22	A	99.7	395	A	A	B	B
Example 3	Sintered body	Ti-6Al-4V	α+β	24	78	2.2	22	32	A	99.5	360	B	B	B	B
Example 4	Sintered body	Ti-6Al-4V	α+β	8	92	1.3	8	18	A	99.6	410	B	B	B	B
Example 5	Sintered body	Ti-6Al-4V	α+β	28	72	2.5	28	38	B	99.3	340	C	C	B	B
Example 6	Sintered body	Ti-6Al-4V	α+β	5	85	1.9	15	25	B	99.1	425	B	C	B	B
Comp. Ex. 1	Sintered body	Ti-6Al-4V	α+β	2	77	1.4	23	33	C	98.5	400	D	D	C	B
Comp. Ex. 2	Sintered body	Ti-6Al-4V	α+β	35	71	4.5	29	51	D	96.4	230	D	E	C	B
Comp. Ex. 3	Sintered body	Ti-6Al-4V	α+β	27	66	7.6	34	63	D	97.2	240	D	E	C	B
Ref. Ex. 1	Ingot material	Ti-6Al-4V	α+β	4	90	3.1	10	20	B	99.8	350	D	C	C	B
Ref. Ex. a	Sintered body	SUS316L	-	-	-	-	-	-	-	-	-	-	F	A	A
Ref. Ex. b	Cast material	F75	-	-	-	-	-	-	-	-	-	-	C	C	-

(continued)

	Production method	Structure of titanium sintered body								Evaluation results						
		Composition	Crystal structure	α-phase			β-phase	X-ray diffraction peak ratio	Specularity	Relative density	Vickers hardness	Wear resistance	Tensile strength	Elongation at break	Cytotoxicity test
				Average grain size	Area ratio	Aspect ratio	Area ratio								
	-	-	-	μm	%	-	%	%	-	%	-	-	-	-	-
Ref. Ex. c	Sintered body	F75	-	-	-	-	-	-	-	-	-	-	D	D	B
Ref. Ex. d	Sintered body	α-Ti	α	5	99.9	2.4	0.1	-	D	96.5	210	E	E	E	B
Negative control material									-						A
Positive control material									-						C

Table 2

	Production method	Structure of titanium sintered body								Evaluation results						
		Composition	Crystal structure	α-phase			β-phase	X-ray diffraction peak ratio		Specularity	Relative density	Vickers hardness	Wear resistance	Tensile strength	Elongation at break	Cytotoxicity test
				Average grain size	Area ratio	Aspect ratio	Area ratio									
	-	-	-	μm	%	-	%	%		-	%	-	-	-	-	-
Example 7	Sintered body	Ti-3Al-2.5V	α+β	18	83	2.0	17	27		A	99.8	370	A	A	B	B
Example 8	Sintered body	Ti-3Al-2.5V	α+β	11	89	1.7	11	21		A	99.7	380	A	A	B	B
Example 9	Sintered body	Ti-3Al-2.5V	α+β	25	79	2.3	21	31		A	99.5	350	A	B	B	B
Example 10	Sintered body	Ti-3Al-2.5V	α+β	9	93	1.4	7	17		A	99.4	400	B	B	B	B
Example 11	Sintered body	Ti-3Al-2.5V	α+β	27	73	2.6	27	37		B	99.2	330	C	C	B	B
Example 12	Sintered body	Ti-3Al-2.5V	α+β	6	84	2.3	16	26		B	99.1	415	B	C	B	B
Comp. Ex. 4	Sintered body	Ti-3Al-2.5V	α+β	2	75	1.7	25	35		C	98.6	390	D	D	C	B
Comp. Ex. 5	Sintered body	Ti-3Al-2.5V	α+β	36	72	4.8	28	52		D	96.5	220	D	E	C	B
Comp. Ex. 6	Sintered body	Ti-3Al-2.5V	α+β	28	68	8.2	32	64		D	97.8	230	D	E	C	B
Ref. Ex. 2	Ingot material	Ti-3Al-2.5V	α+β	3	91	3.2	9	19		B	99.7	340	D	C	C	B

Table 3

	Production method	Structure of titanium sintered body							Evaluation results						
		Composition	Crystal structure	α-phase			β-phase	X-ray diffraction peak ratio	Specularity	Relative density	Vickers hardness	Wear resistance	Tensile strength	Elongation at break	Cytotoxicity test
				Average grain size	Area ratio	Aspect ratio	Area ratio								
	-	-	-	μm	%	-	%	%	-	%	-	-	-	-	-
Example 13	Sintered body	Ti-6Al-7Nb	α+β	13	90	1.9	10	20	A	99.7	390	A	A	B	A
Example 14	Sintered body	Ti-6Al-7Nb	α+β	9	96	1.5	4	14	A	99.8	400	A	A	B	A
Example 15	Sintered body	Ti-6Al-7Nb	α+β	22	80	2.1	20	30	A	99.3	360	B	B	B	A
Example 16	Sintered body	Ti-6Al-7Nb	α+β	7	98	1.3	2	12	A	99.5	420	A	B	B	A
Example 17	Sintered body	Ti-6Al-7Nb	α+β	25	78	2.2	22	32	B	99.0	340	C	C	B	A
Example 18	Sintered body	Ti-6Al-7Nb	α+β	5	92	1.8	8	18	B	99.2	440	B	C	B	A
Comp. Ex. 7	Sintered body	Ti-6Al-7Nb	α+β	2	76	1.6	24	34	C	98.4	410	D	D	C	A
Comp. Ex. 8	Sintered body	Ti-6Al-7Nb	α+β	37	71	4.9	29	53	D	96.6	210	D	E	C	A
Comp. Ex. 9	Sintered body	Ti-6Al-7Nb	α+β	29	65	7.8	35	65	D	97.6	220	D	E	C	A
Ref. Ex. 3	Ingot material	Ti-6Al-7Nb	α+β	4	93	3.5	7	17	B	99.5	330	D	B	C	A

[0175] As apparent from Tables 1 to 3, it was confirmed that the titanium sintered bodies of the respective Examples have high specularity on the polished surface. Further, since the relative density and the Vickers hardness are also high, it was confirmed that the titanium sintered bodies of the respective Examples can maintain high specularity for a long period of time.

[0176] It was also confirmed that the characteristics such as specularity, density, and hardness of the titanium sintered bodies of the respective Examples are equivalent to or higher than those of the titanium ingot materials. Therefore, according to the invention, a titanium sintered body having excellent characteristics can be obtained while taking advantage of the characteristic of near-net shape.

[0177] An electron microscopic image of a cross section of the titanium sintered body of Comparative Example 2 is shown in FIG. 6. From FIG. 6, it is confirmed that in the titanium sintered body of Comparative Example 2, the α-phase has an elongated shape, that is, a shape with large anisotropy.

[0178] Further, an electron microscopic image of a cross section of the titanium ingot material of Reference Example 1 is shown in FIG. 7. From FIG. 7, it is confirmed that in the titanium ingot material of Reference Example 1, although the grain size of the α-phase is relatively small, the α-phase has a shape with large anisotropy.

Claims

1. A titanium sintered body comprising an α-phase and a β-phase as crystal structures, wherein the average cross-sectional grain size of the α-phase is 3-30 μm, and wherein the α-phase occupies 70-99.8% of the cross sectional area of the sintered body.

2. The titanium sintered body according to claim 1, wherein the average aspect ratio of the α-phase in a cross section is 1-3.

3. The titanium sintered body according to claim 1, wherein, in the X-ray diffraction spectrum, the value of the peak reflection intensity by the plane orientation (110) of the β-phase is 3-60% of the value of the peak reflection intensity by the plane orientation (100) of the α-phase.

4. The titanium sintered body according to claim 1, wherein the titanium sintered body comprises titanium as a main component, and further comprises an α-phase stabilizing element and a β-phase stabilizing element.

5. The titanium sintered body according to claim 1, wherein the titanium sintered body has a relative density of 99% or more.

6. An ornament comprising the titanium sintered body according to any preceding claim.

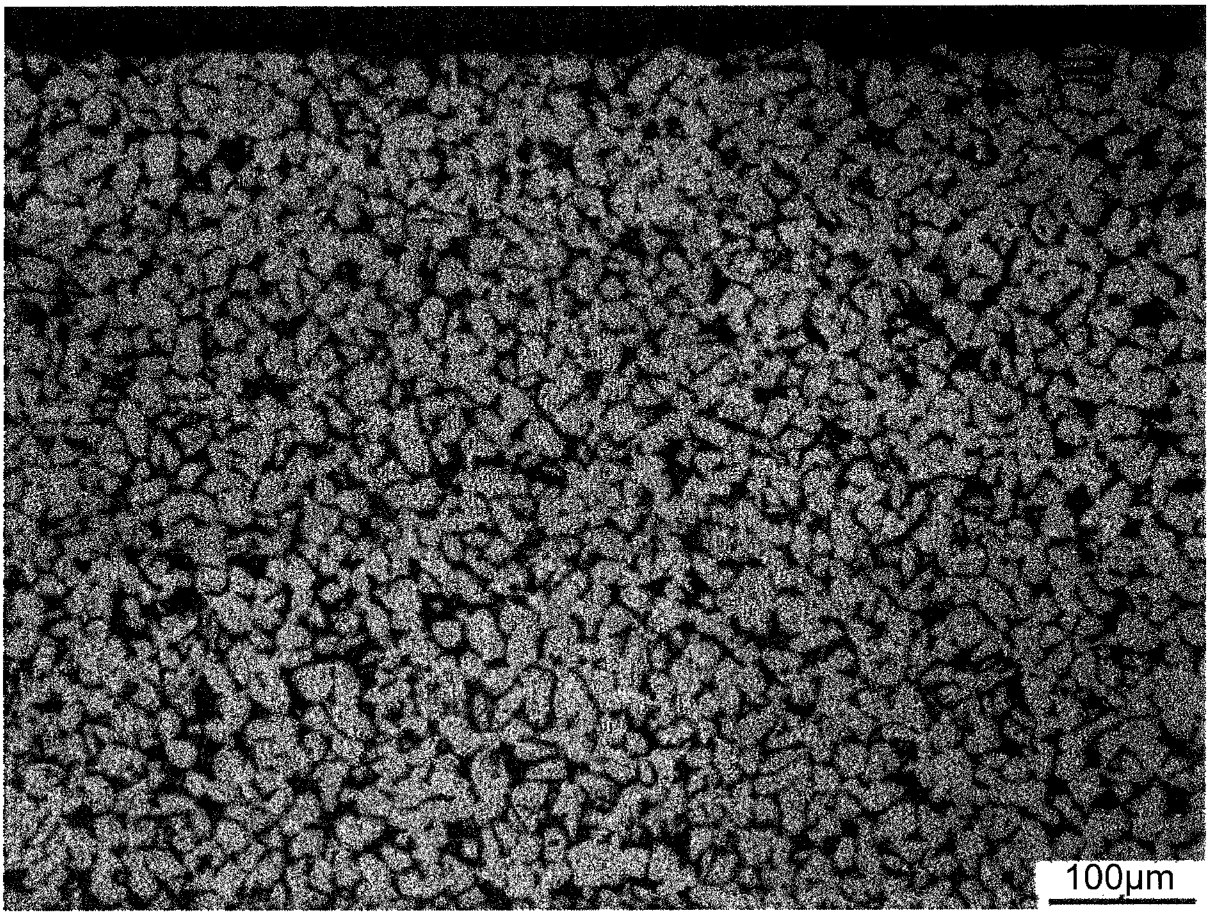

FIG. 1

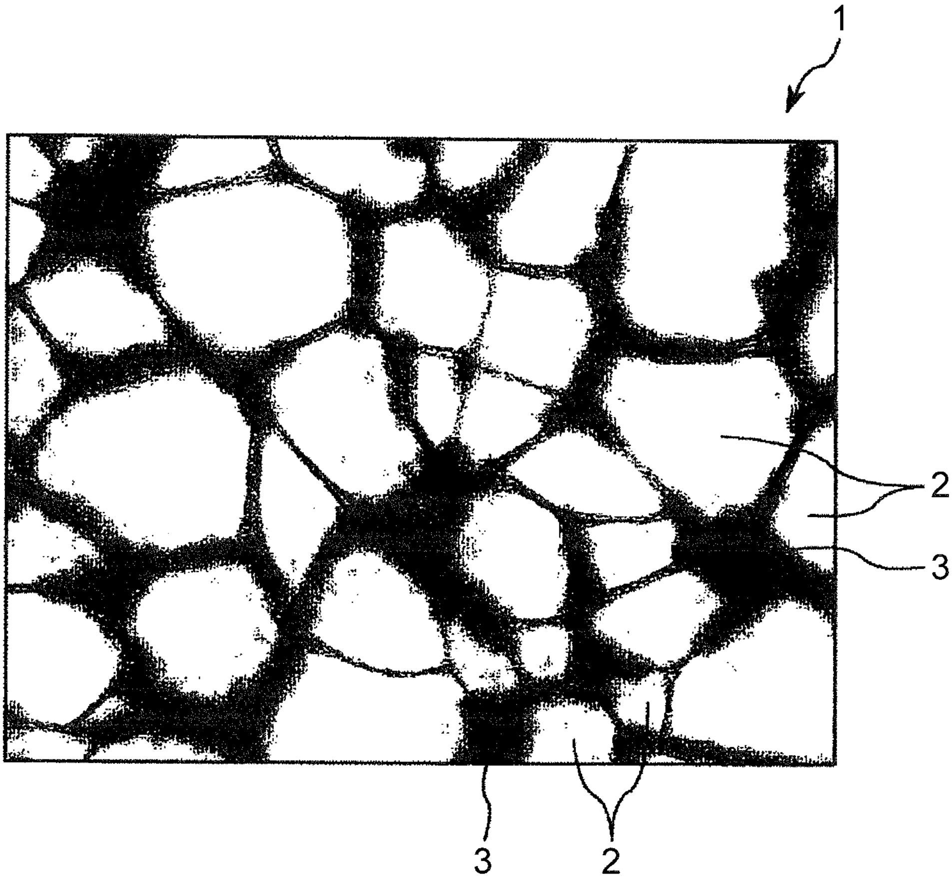

FIG. 2

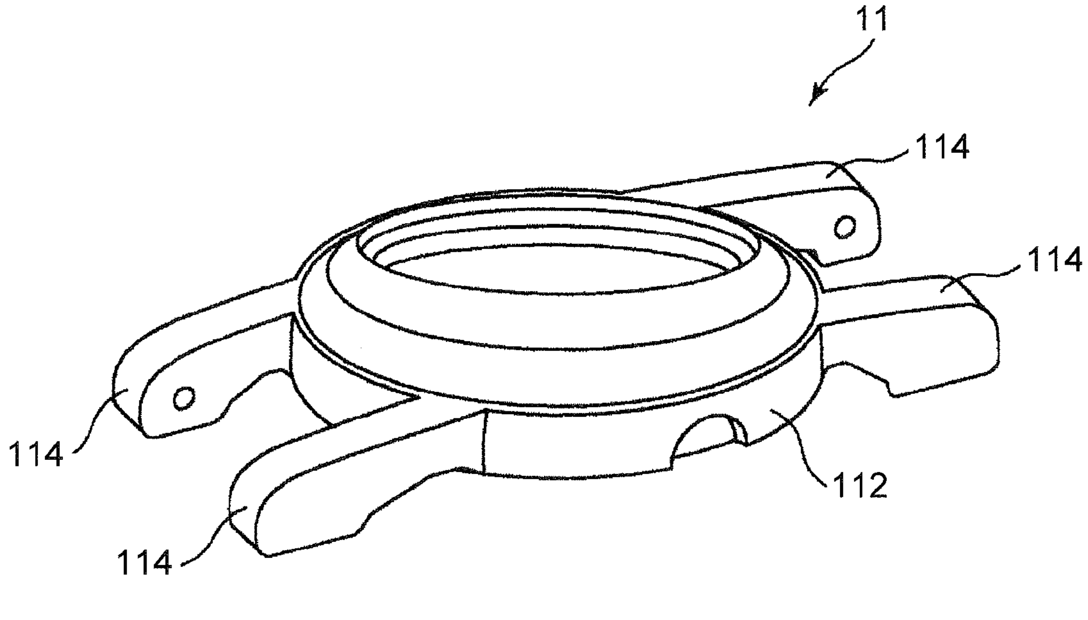

FIG. 3

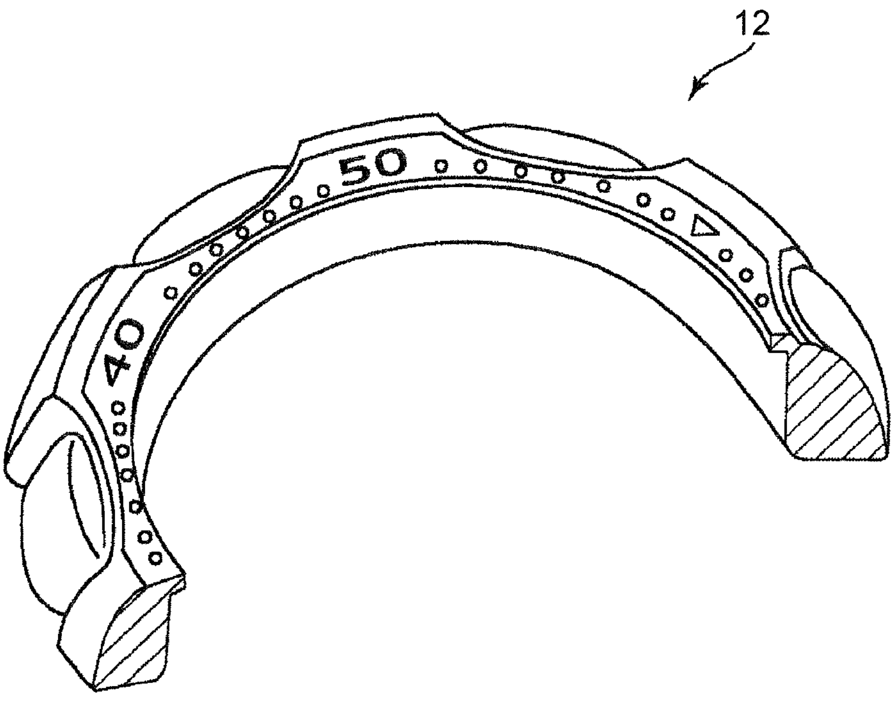

FIG. 4

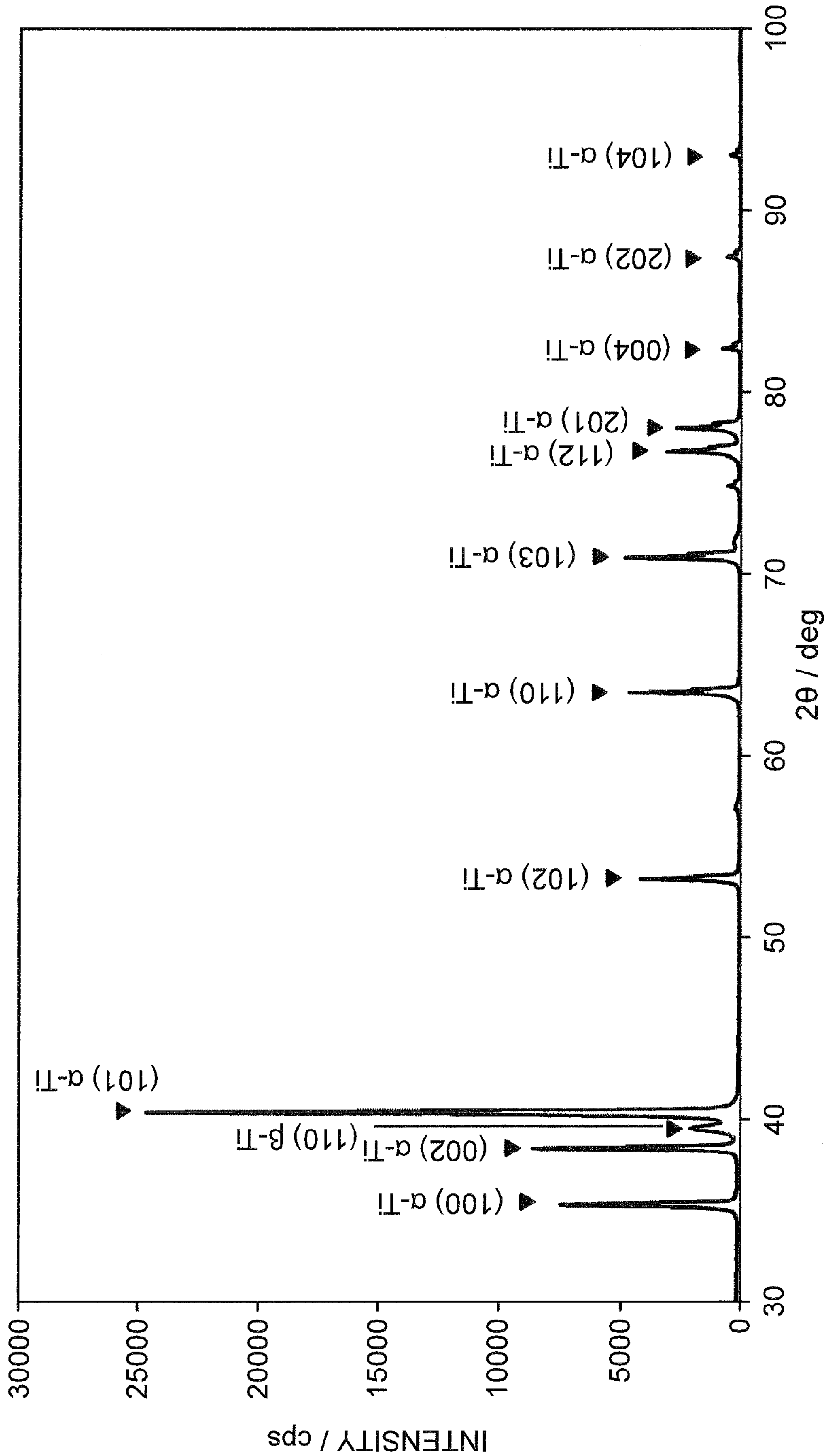
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FIG. 5

FIG. 6

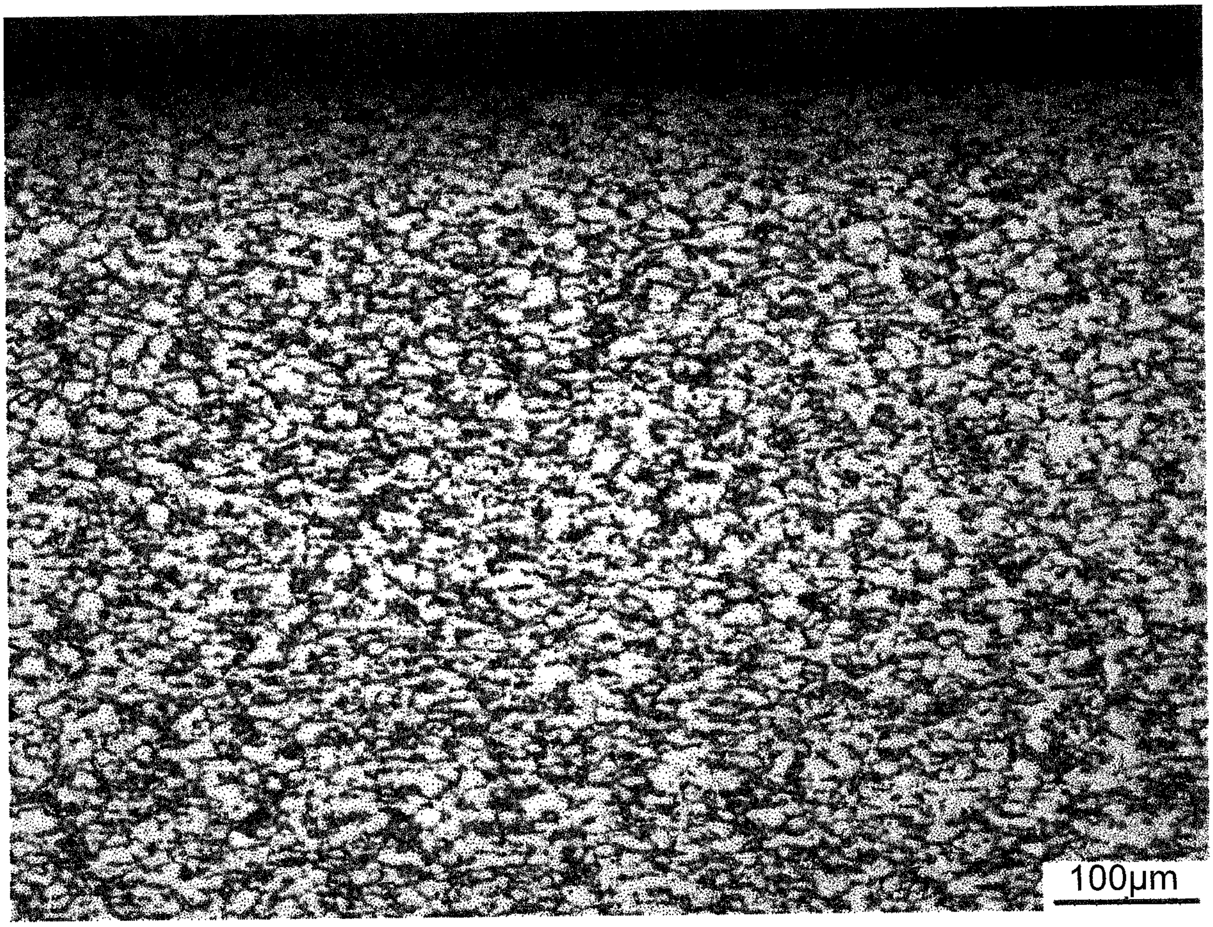

FIG. 7

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EUROPEAN SEARCH REPORT

Application Number
EP 16 18 7193

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2011/277891 A1 (CLEMENS HELMUT [AT] ET AL) 17 November 2011 (2011-11-17) * paragraphs [0008], [0100], [0113]; claims 1,15 *	1-4,6	INV. A43C11/24 C22C14/00 G04B37/00 G04B37/22 A44C25/00 B22F5/10 ADD. C22C1/04 B22F1/00
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The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
The Hague	31 January 2017	Aliouane, Nadir

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31-01-2017

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