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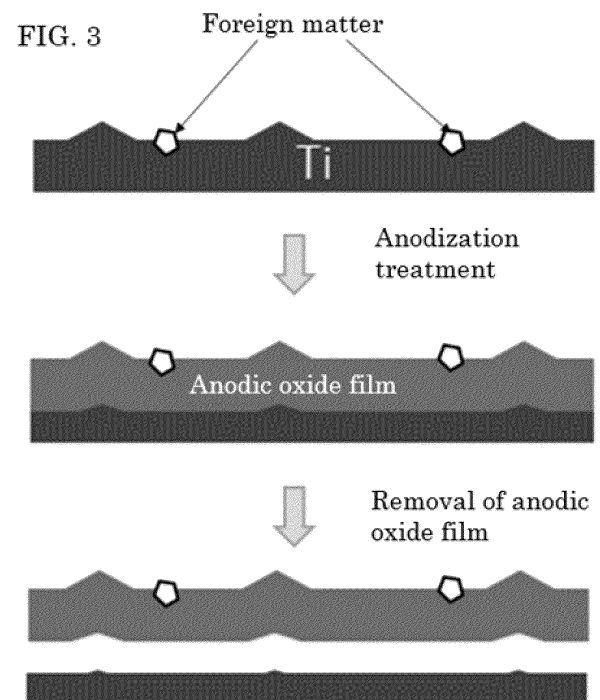
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(54) **SURFACE-SMOOTHENED METAL MEMBER AND METHOD FOR MANUFACTURING SAME**

(57) Provided are a surface-smoothened metal member and a method for easily and effectively manufacturing the same, said surface-smoothened metal member having been smoothened to such an extent that in a surface of a large metal member formed from titanium or a titanium alloy, a flat surface portion has a maximum height roughness (Rz) of 1.1 μm or less and a portion with a curvature radius of 0.05 to 2.5 mm has a maximum height roughness (Rz) of less than 2 μm . This method for manufacturing the surface-smoothened metal member is characterized in that an anodic oxide film is formed on a surface of a substrate formed from titanium or a titanium alloy by applying an anodization treatment to the substrate, and the surface of the substrate is smoothened by removing the anodic oxide film.



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Description

TECHNICAL FIELD

- 5 **[0001]** The present invention relates to a metal member made of titanium or a titanium alloy that is required to have a smoothened surface, and a method for manufacturing the same.

PRIOR ARTS

- 10 **[0002]** In addition to being lightweight, titanium and titanium alloys have excellent corrosion resistance and high specific strength, and are used in a variety of applications, including structural members for aircrafts and bicycles, engine parts, optical members, electronic parts, and decorative items.

- [0003]** Here, the condition of the surface of members is often considered important, particularly in optical members and decorative items, and methods for smoothening the surface of members made of titanium or the titanium alloys have been investigated.

- 15 **[0004]** For example, Patent Literature 1 (JP 2008-223139 A) discloses, in the method of electropolishing and/or electrochemical deburring of the surface of titanium or a titanium-containing alloy, a method for electrolytic polishing and/or electrochemical deburring of the surface of titanium or a titanium-containing alloy, characterized in that the electrolyte used comprises methanesulfonic acid and one or more alkanediphosphonic acids, and the one or more alkanediphosphonic acids can optionally be substituted with hydroxy and/or amino groups.

- 20 **[0005]** In the method of method for electrolytic polishing and/or electrochemical deburring described in Patent Literature 1, it is said that the electrolyte used is not combustible, is not especially corrosive and is easy to handle, and with normal handling, there is no increased risk for the people operating the electropolishing plant or working in the vicinity of this plant, or for the environment. In particular, the electrolyte described here does not release any harmful gases or vapors.

- 25 **[0006]** Further, Patent Literature 2 (JP 2004-43850 A) discloses a method for etching titanium or a titanium alloy, which is characterized by treating the titanium or titanium alloy with an aqueous solution containing (a) 5 to 30 weight of hydrogen peroxide, (b) 1 to 20 weight of a fluoride, (c) 1 to 10 % by weight of at least one acid selected from sulfuric acid, nitric acid, and phosphoric acid, and (d) 0.001 to 0.1 % by weight of a fluorine-containing surfactant, and in which the weight ratio of [(a) hydrogen peroxide concentration]/[(b) fluoride concentration of the fluoride] is 1.5 to 3.0.

- 30 **[0007]** In the method for etching titanium or a titanium alloy described in the Patent Literature 2, it is said that by etching with the aqueous solution containing hydrogen peroxide, the fluoride, the inorganic acid, and the fluorine-containing surfactant, it is possible to simultaneously remove surface scale from the titanium or titanium alloy and smoothen the surface.

35 CITATION LIST

Patent Literature

[0008]

- 40 Patent Literature 1: JP 2008-223139 A
Patent Literature 2: JP 2004-43850 A

SUMMARY OF INVENTION

45 Technical Problem

- [0009]** However, the method for electrolytic polishing and/or electrochemical deburring described in the Patent Literature 1 provides a good working environment, but, as stated that "can achieve surface smoothening or deburring that is at least as good as, if not better than, that of the methods described in the prior art", the smoothness is not improved as compared to the prior art.

- 50 **[0010]** Further, the etching method for titanium or a titanium alloy described in Patent Literature 2 can simultaneously achieve surface scale removal and smoothening, but the surface roughness obtained by smoothening is around 0.4 μm , which is not suitable for cases where higher smoothness is required.

- 55 **[0011]** Furthermore, the methods described in Patent Literature 1 and Patent Literature 2 only provide a relatively narrow area having a good smooth surface, and it is difficult to efficiently reduce foreign matter and achieve a mirror finish over the entire surface of a large metal member. Further, when the metal member has corners with an extremely small radius of curvature, or when the metal member has openings or through holes, it is extremely difficult to smoothen these

inner surfaces.

[0012] In view of the problems in the prior arts as described above, the object of the present invention is to provide, in a large metal member made of titanium or a titanium alloy, a surface-smoothened metal member in which the surface is smoothened to such an extent that a maximum height roughness (Rz) of a flat surface portion of the metal member is 1.1 pm or less, and a maximum height roughness (Rz) of a portion of the surface of the metal member having a radius of curvature of 0.05 to 2.5 mm is less than 2 μm ; and a simple and efficient method for manufacturing the same.

[0013] Further, another object of the present invention is to provide a surface-smoothened metal member in which, even in the case of a large metal member made of titanium or a titanium alloy or a metal member having an opening or through hole, a maximum height roughness (Rz) of the inner wall of the through hole or opening is smoothened to an extent of less than 2 μm ; and a simple and efficient method for manufacturing the same.

Solution to Problem

[0014] In order to achieve the above object, the inventors have done extensive study to methods for smoothening the surface of the metal member made of titanium or a titanium alloy, and have found that detaching an anodic oxide film formed under appropriate conditions is extremely effective, and then have reached the present invention.

[0015] Namely, the present invention also provides a surface-smoothened metal member comprising titanium or a titanium alloy, characterized in that:

a maximum length of the metal member is 50 to 1000 mm;
a maximum height roughness (Rz) of a flat surface portion of the metal member is 1.1 pm or less; and
a maximum height roughness (Rz) of a portion of the surface of the metal member having a radius of curvature of 0.05 to 2.5 mm is less than 2 pm.

[0016] It is preferable that a maximum length of the metal member is 50 to 1000 mm, and more preferably 100 to 500 mm. It is difficult to smooth the entire surface of a large metal member by using conventionally known methods, but in the surface-smoothened metal member of the present invention, even in the metal members having a maximum length of 50 mm or more, the maximum height roughness (Rz) of a flat surface portion is 1.1 pm or less and the maximum height roughness (Rz) of a portion of the surface of the metal member having a radius of curvature of 0.05 to 2.5 mm is less than 2 pm. Further, by setting the maximum length of the metal member to 1000 mm or less, the maximum height roughness (Rz) of the portion having a radius of curvature of 0.05 to 2.5 mm can be exactly set to less than 2 pm.

[0017] It is preferable that the surface-smoothened metal member of the present invention has a through hole and/or an opening in the metal member, and that a maximum height roughness (Rz) of the inner wall of the through holes and/or the openings is also less than 2 pm. In conventional surface-smoothened metal members, the areas where a satisfactory smooth surface is formed are limited, and it is particularly difficult to smooth the inner wall of the through hole and openings, but, in the surface-smoothened metal member of the present invention, the entire surface is sufficiently smoothened.

[0018] The present invention also provides a surface-smoothened metal member comprising titanium or a titanium alloy, characterized in that

a maximum length of the metal member is 50 to 1000 mm;
an arithmetic mean roughness (Ra) of a portion of the surface of the metal member having a radius of curvature of 0.05 to 2.5 mm is less than 0.4 pm.

[0019] It is preferable that a maximum length of the metal member is 50 to 1000 mm, and more preferably 100 to 500 mm. It is difficult to smooth the entire surface of a large metal member by using conventionally known methods, but in the surface-smoothened metal member of the present invention, even in the metal members having a maximum length of 50 mm or more, the arithmetic mean roughness (Ra) of a portion of the surface of the metal member having a radius of curvature of 0.05 to 2.5 mm is less than 0.4 pm. Further, by setting the maximum length of the metal member to 1000 mm or less, the arithmetic mean roughness (Ra) of the portion having a radius of curvature of 0.05 to 2.5 mm can be exactly set to less than 0.4 pm.

[0020] It is preferable that the surface-smoothened metal member of the present invention has a through hole and/or an opening in the metal member, and that the arithmetic mean roughness (Ra) of the inner wall of the through hole and/or the opening is also less than 0.4 pm. In conventional surface-smoothened metal members, the areas where a satisfactory smooth surface is formed are limited, and it is particularly difficult to smooth the inner wall of the through hole and openings, but, in the surface-smoothened metal member of the present invention, the entire surface is sufficiently smoothened.

[0021] In the surface-smoothened metal member of the present invention, it is preferable that an equivalent circle

diameter of the through hole and/or the opening is 0.1 to 5 mm. The more preferable equivalent circle diameter is 0.2 to 2 mm, and the most preferable equivalent circle diameter is 0.5 to 1 mm. In the surface-smoothened metal member of the present invention, even when minute through hole and/or opening having the equivalent circle diameter of 5 mm or less are formed, it is possible to reduce the arithmetic mean roughness (Ra) and the maximum height roughness (Rz) of the inner surface sufficiently. Further, when the equivalent circle diameter of the through hole and/or opening is 0.1 mm or more, it is possible to reduce the variation in the arithmetic mean roughness (Ra) and the maximum height roughness (Rz) of the inner wall.

[0022] In the surface-smoothened metal member of the present invention, it is preferable that a depth of the through hole and/or the opening is 1 to 50 mm. The more preferable depth of the opening is 1 to 10 mm, and the most preferable depth of the opening is 2 to 8 mm. In the surface-smoothened metal member of the present invention, even when deep through hole and/or opening having the depth of 1 mm or more are formed, it is possible to reduce the arithmetic mean roughness (Ra) and the maximum height roughness (Rz) of the inner surface sufficiently. Further, when the depth of the through hole and/or opening is 50 mm or less, it is possible to reduce the variation in the arithmetic mean roughness (Ra) and the maximum height roughness (Rz) of the inner wall.

[0023] In the surface-smoothened metal member of the present invention, it is preferable that the metal member is a frame body.

By using the metal member as the frame body, it can be suitably used as, for example, a pellicle frame.

[0024] The present invention also provides a method for manufacturing a surface-smoothened metal member, comprising:

subjecting a substrate made of titanium or a titanium alloy to anodization treatment to form an anodic oxide film on the surface of the substrate; and
smoothing the surface of the substrate by detaching the anodic oxide film.

[0025] In the method for manufacturing a surface-smoothened metal member of the present invention, the convex portions of the substrate surface (metal member surface) are consumed by the formation of the anodic oxide film to progress the smoothing, and the smoothed surface can be obtained by detaching the anodic oxide film. In addition, since foreign matters adhering to the surface of the substrate are removed by the detachment of the anodic oxide film, a clean surface can be obtained. Furthermore, the anodic oxide film can also be formed on a large substrate, making it possible to smoothen the surface of a large metal member.

[0026] Further, in the method for manufacturing a surface-smoothened metal member of the present invention, it is preferable that a thickness of the anodic oxide film is 2 to 10 μm . More preferably, by setting the thickness of the anodic oxide film to 4 to 6 μm , not only are the convex portions on the surface of the substrate efficiently consumed, but the anodic oxide film can be naturally detached without the need for any special process.

[0027] Further, in the method for manufacturing a surface-smoothened metal member of the present invention, it is preferable that a voltage applied in the anodization treatment is 20 to 100 V. The anodization treatment conditions are not particularly limited as long as the effects of the present invention are not impaired, and various conventionally known treatment conditions can be used, more preferably, by setting the applied voltage to 40 to 50 V, not only are the convex portions on the surface of the substrate efficiently consumed, but the anodic oxide film can be naturally detached without the need for any special process.

[0028] Furthermore, in the method for manufacturing a surface-smoothened metal member of the present invention, it is preferable to repeat the formation and detachment of the anodic oxide film until the arithmetic mean roughness (Ra) of less than 0.4 μm and/or the maximum height roughness (Rz) of less than 2 μm is obtained on the surface of the substrate.

[0029] Since the formation and detachment of the anodic oxide film leads to the smoothing of the substrate surface, by repeating this process, it is possible to reliably obtain the arithmetic mean roughness (Ra) of less than 0.4 μm and/or the maximum height roughness (Rz) of less than 2 μm on the substrate surface.

EFFECT OF THE INVENTION

[0030] According to the present invention, it is possible to provide, in a large metal member made of titanium or a titanium alloy, a surface-smoothened metal member in which the surface is smoothed to such an extent that a maximum height roughness (Rz) of a flat surface portion of the metal member is 1.1 μm or less, and a maximum height roughness (Rz) of a portion of the surface of the metal member having a radius of curvature of 0.05 to 2.5 mm is less than 2 μm ; and a simple and efficient method for manufacturing the same. Further, according to the present invention, it is possible to provide a surface-smoothened metal member in which, even in the case of a large metal member made of titanium or a titanium alloy or a metal member having an opening or through hole, a maximum height roughness (Rz) of the inner wall of the through hole or opening is smoothed to an extent of less than 2 μm ; and a simple and efficient method for manufacturing the same.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031]

FIG. 1 is a schematic view of the pellicle frame, which is one embodiment of the surface-smoothened metal member of the present invention.

FIG. 2 is a cross-sectional view of B-B' in FIG. 1.

FIG. 3 is a schematic diagram of the surface-smoothing process in the present invention.

FIG. 4 is SEM photographs of the surface of the substrate for the pellicle frame before the anodization treatment, the surface of the anodic oxide film, and the surface of the substrate for the pellicle frame from which the anodic oxide film has been detached.

FIG. 5 is a SEM photograph of the cross section of the detached anodic oxide film and the substrate for the pellicle frame.

FIG. 6 is SEM photographs, in the case when the anodization treatment is performed at each voltage, of the surface of the substrate for the pellicle frame from which the anodic oxide film has been detached, the surface of the anodic oxide film, and a cross section of the anodic oxide film.

FIG. 7 is SEM photograph of the side surface of the through hole before anodization treatment and after detachment of the anodic oxide film.

FIG. 8 is a schematic diagram showing measurement lines of the maximum height roughness (Rz) and the arithmetic mean roughness (Ra).

FIG. 9 is microscopically observing images of the surface of the pure titanium rectangular bar before and after the anodization treatment.

FIG. 10 is microscopically observing images of the inner surface of the through hole before and after the anodization treatment.

FIG. 11 is SEM photographs of the inner surface of the through hole before and after the anodization treatment.

Embodiments for achieving the invention

[0032] Hereinafter, a pellicle frame will be taken up as a typical embodiment of the surface-smoothened metal member, typical embodiments of the surface-smoothened metal member and the manufacturing method thereof according to the present invention will be described in detail with reference to the drawings, but the present invention is not limited to only these examples. Further, the elements in the embodiment can be optionally combined with a part or the whole. In the following description, the same or equivalent parts are denoted by the same numerals, and there is a case that redundant explanation may be omitted. In addition, since the drawings are for conceptually explaining the present invention, dimensions of the respective constituent elements expressed and ratios thereof may be different from actual ones.

1. Surface-smoothened metal member

[0033] FIG. 1 shows a schematic view of a pellicle frame, which is one embodiment of the surface-smoothened metal member of the present invention. The pellicle frame 1 is made of titanium or a titanium alloy, and all of its surfaces are smoothened.

[0034] The maximum length of the pellicle frame 1 is 50 to 1000 mm.

Here, the maximum length of the pellicle frame 1 is the length of the diagonal line indicated by A in FIG. 1. The maximum length is preferably from 100 to 500 mm, and more preferably from 150 to 300 mm. It is difficult to smoothen the entire surface of a large metal member by using conventionally known methods, but in the surface-smoothened metal member of the present invention, even in the pellicle frame 1 having a maximum length of 50 mm or more, the maximum height roughness (Rz) of a flat surface portion is 1.1 μm or less and the maximum height roughness (Rz) of a portion of the surface of the metal member having a radius of curvature of 0.05 to 2.5 mm is less than 2 μm . Further, by setting the maximum length of the pellicle frame 1 to 1000 mm or less, the maximum height roughness (Rz) of the portion having a radius of curvature of 0.05 to 2.5 mm can be exactly set to less than 2 μm .

[0035] Further, in the pellicle frame 1, even in the maximum length of 50 mm or more, the arithmetic mean roughness (Ra) of a portion of the surface having a radius of curvature of 0.05 to 2.5 mm is less than 0.4 μm . Further, by setting the maximum length to 1000 mm or less, the arithmetic mean roughness (Ra) of the portion having a radius of curvature of 0.05 to 2.5 mm can be exactly set to less than 0.4 μm .

[0036] It is preferable that the pellicle frame 1 has a through hole and/or an opening, and that the maximum height roughness (Rz) of the inner walls of the through hole and/or the opening is less than 2 μm and the arithmetic mean roughness (Ra) is less than 0.4 μm . FIG. 1 shows a case where the through hole 2 is present, and FIG. 2 shows a cross-sectional view taken along line B-B' of FIG. 1. The inner surface of the through hole 2 indicated by the dotted line is also

sufficiently smoothened, and the maximum height roughness (R_z) is less than 2 μm and the arithmetic mean roughness (R_a) is less than 0.4 μm .

[0037] It is preferable that an equivalent circle diameter (R in FIG. 2) of the opening of the through hole 2 is 0.1 to 5 mm. The more preferable equivalent circle diameter is 0.2 to 2 mm, and the most preferable equivalent circle diameter is 0.5 to 1 mm. In the pellicle frame 1, even when minute through hole 2 having the equivalent circle diameter of 5 mm or less are formed, it is possible to reduce the arithmetic mean roughness (R_a) and the maximum height roughness (R_z) of the inner surface sufficiently. Further, when the equivalent circle diameter of the through hole 2 is 0.1 mm or more, it is possible to reduce the variation in the arithmetic mean roughness (R_a) and the maximum height roughness (R_z) of the inner wall.

[0038] Further, it is preferable that a depth (D in FIG. 2) of the through hole 2 is 1 to 50 mm. The more preferable depth of the through hole 2 is 1 to 10 mm, and the most preferable depth of the through hole 2 is 2 to 8 mm. In the pellicle frame 1, even when deep through hole having the depth of 1 mm or more are formed, it is possible to reduce the arithmetic mean roughness (R_a) and the maximum height roughness (R_z) of the inner surface sufficiently. Further, when the depth of the through hole 2 is 50 mm or less, it is possible to reduce the variation in the arithmetic mean roughness (R_a) and the maximum height roughness (R_z) of the inner wall.

[0039] The shape of the pellicle frame 1 is not particularly limited as long as the effect of the present invention is not impaired, and various conventionally known shapes can be used depending on the shape of the light exposure original plate, and in general, the planar shape of the pellicle frame 1 is a ring shape, a rectangular shape, or a square shape, and has a size and a shape that cover a circuit pattern portion provided on the light exposure original plate.

[0040] The height (thickness) of the pellicle frame 1 is preferably 0.5 to 10 mm, more preferably 1 to 7 mm, and most preferably 1.0 to 3.0 mm. By setting the height (thickness) of the pellicle frame 1 to these values, deformation of the pellicle frame body 1 can be suppressed and good handleability can be ensured.

[0041] The cross-sectional shape of the pellicle frame 1 is not particularly limited as long as the effect of the present invention is not impaired, and may be various conventionally known shapes, and preferable is a quadrilateral where the upper side and the lower side are parallel. The upper side of the pellicle frame 1 needs a width for stretching the pellicle film, and the lower side needs a width for providing an adhesive layer for adhesion and adhering to the light exposure original plate. For this reason, the width of the upper side and the lower side of the pellicle frame 1 is preferably around 1 to 3 mm.

[0042] Since the pellicle frame 1 is made of titanium or a titanium alloy, the strength and Young's modulus are higher than those of the conventionally used pellicle frames made of aluminum alloys. Further, since titanium and titanium alloys are relatively light having a specific gravity of approximately 4.5, making it possible to suppress an increase in the weight of the pellicle frame 1.

[0043] Further, since the pellicle frame 1 is made of titanium or a titanium alloy, the linear expansion coefficient is lower than that of aluminum, and distortion during temperature rise is effectively suppressed. Further, since titanium and titanium alloys are metallic materials and have superior toughness compared to ceramics and cemented carbide, making them easy to handle. Furthermore, due to a good processability, the manufacturing cost can be reduced, and in addition, the pellicle frame 1 can be given high dimensional accuracy.

[0044] Further, when the surface-smoothened metal member of the present invention is used for various optical members, it is preferable that a linear expansion coefficient of the optical member is preferably 6×10^{-6} to $11 \times 10^{-6}/\text{K}$. By setting the linear expansion coefficient to $6 \times 10^{-6}/\text{K}$ or more, the thermal expansion coefficient of the optical member becomes close to that of a material made of ceramic, silicon, or the like. This makes it possible to reduce distortion and cracking caused by the difference in deformation due to thermal expansion when the temperature rises between the optical member and the member made of ceramic, silicon, or the like. As a combination to provide such an effect, for example, there is a case that the optical member is a lens holder and the member made of ceramic, silicon, or the like is a lens for a camera or the like. Further, by setting the linear expansion coefficient to $11 \times 10^{-6}/\text{K}$ or less, distortion during temperature rise can be reduced. A more preferable linear expansion coefficient is 7×10^{-6} to $10 \times 10^{-6}/\text{K}$, and a most preferable linear expansion coefficient is 8×10^{-6} to $9 \times 10^{-6}/\text{K}$. In this description, the linear expansion coefficient is expressed as a value in the temperature range of 0 to 100°C. These linear expansion coefficients can be achieved, for example, by making the optical member from titanium or a titanium alloy.

[0045] The titanium alloy used for the pellicle frame 1 is not particularly limited as long as the effect of the present invention is not impaired, and various conventionally known titanium alloys can be used. Examples of the titanium alloys include Ti-6Al-4V alloy, Ti-6Al-6V-2Sn alloy, Ti-6Al-2Sn-4Zr-6Mo alloy, Ti-10V-2Fe-3Al alloy, Ti-7Al-4Mo alloy, Ti-5Al-2.5Sn alloy, Ti-6Al-5Zr-0.5Mo-0.2Si alloy, Ti-5.5Al-3.5Sn-3Zr-0.3Mo-1Nb-0.3Si alloy, Ti-8Al-1Mo-1V alloy, Ti-6Al-2Sn-4Zr-2Mo alloy, Ti-5Al-2Sn-2Zr-4Mo-4Cr alloy, Ti-11.5Mo-6Zr-4.5Sn alloy, Ti-15V-3Cr-3Al-3Sn alloy, Ti-15Mo-5Zr-3Al alloy, Ti-15Mo-5Zr alloy, and Ti-13V-11Cr-3Al alloy.

[0046] When workability and corrosion resistance are important, it is preferable to use pure titanium, and from the viewpoint of achieving both high strength and good workability, it is preferable to use an $\alpha+\beta$ type alloy, and further, furthermore, from the viewpoints of material price and availability, it is more preferable to use a Ti-6Al-4V alloy.

[0047] In the above embodiment, the pellicle frame 1 has been described as an example of the surface-smoothened metal member, but the surface-smoothened metal member is not limited thereto. For example, various optical members

may be produced, and examples are the pellicle frame, a lens holder, a barrel, a shade, a reflector, and the like.

2. Manufacturing method for surface-smoothened metal member

[0048] When manufacturing the pellicle frame 1 having a smoothened surface by using the manufacturing method for a surface-smoothened metal member of the present invention, a frame body made of titanium or a titanium alloy is subjected to anodization treatment to form an anodic oxide film on the surface of the frame body, and the surface of the frame body is smoothened by removing the anodic oxide film.

[0049] FIG. 3 shows a schematic diagram of the surface smoothing process. The convex portions of the surface of the frame body are consumed by the formation of the anodic oxide film to progress the smoothing, and the smoothened surface can be obtained by detaching the anodic oxide film. In addition, since foreign matters adhering to the surface of the frame body are removed by the detachment of the anodic oxide film, a clean surface can be obtained.

[0050] Though it is extremely difficult to uniformly and easily smoothen the surface of a large member by using conventional surface smoothing techniques, by using the anodization treatment, it is possible to smoothen the entire surface of a large pellicle frame 1 having a maximum length of 50 to 1000 mm.

[0051] Further, it is preferable that a thickness of the anodic oxide film formed on the surface of the frame body is 2 to 10 μm . More preferably, by setting the thickness of the anodic oxide film to 4 to 6 μm , not only are the convex portions on the surface of the frame body efficiently consumed, but the anodic oxide film can be naturally detached without the need for any special process. If the anodic oxide film remains, the anodic oxide film may be detached by applying ultrasonic vibrations, reverse electrolysis, or the like.

[0052] Further, it is preferable that a voltage applied in the anodization treatment is 20 to 100 V. The anodization treatment conditions are not particularly limited as long as the effects of the present invention are not impaired, and various conventionally known treatment conditions can be used, more preferably, by setting the applied voltage to 40 to 50 V, not only are the convex portions on the surface of the frame body efficiently consumed, but the anodic oxide film can be naturally detached without the need for any special process.

[0053] Furthermore, when the maximum height roughness (R_z) of the surface of the frame body becomes 2 μm or more after one formation and detachment of the anodic oxide film, it is preferable to repeat the formation and detachment of the anodic oxide film until the value becomes less than 2 μm . Since the formation and detachment of the anodic oxide film leads to the smoothing of the surface of the frame body, by repeating this process, it is possible to reliably obtain the maximum height roughness (R_z) of less than 2 μm on the surface of the substrate.

[0054] Further, when the arithmetic mean roughness (R_a) of the surface of the frame body becomes 0.4 μm or more after one formation and detachment of the anodic oxide film, it is preferable to repeat the formation and detachment of the anodic oxide film until the value becomes less than 0.4 μm . Since the formation and detachment of the anodic oxide film leads to the smoothing of the surface of the frame body, by repeating this process, it is possible to reliably obtain the arithmetic mean roughness (R_a) of less than 0.4 μm on the surface of the substrate.

[0055] The representative embodiments of the present invention have been described above, but the present invention is not limited only to these embodiments, and various design changes are possible, and all such design changes are included in the technical scope of the present invention.

EXAMPLE

<Example 1>

[0056] A frame body having a long side of 160 mm and a short side of 130 mm was cut out from pure titanium to prepare a substrate for a pellicle frame. The thickness and width of the substrate for the pellicle frame are the same, 1 mm and 4 mm, respectively.

[0057] The obtained substrate for the pellicle frame was subjected to the anodization treatment to form an anodic oxide film over the entire surface. The anodization was conducted under the conditions that, as an anodization bath, an aqueous solution which dissolved 5 g/L of ammonium fluoride and 134 g/L of ammonium sulfate, at a bath temperature of 55° C and a voltage of 30 to 80 V for 15 minutes.

[0058] FIG. 4 shows scanning electron microscope (SEM) photographs of the surface of the substrate for the pellicle frame before the anodization treatment, the surface of the anodic oxide film, and the surface of the substrate for the pellicle frame from which the anodic oxide film has been detached, when the voltage set to 45 V. FIG. 5 shows an SEM photograph of the cross section of the detached anodic oxide film and the substrate for the pellicle frame. Here, most of the anodic oxide film naturally peeled off during the anodization treatment.

[0059] It can be seen that the surface of the substrate for the pellicle frame has been significantly smoothened by the detachment of the anodic oxide film, and a good smooth surface completely free of foreign matters has been obtained. Further, it can be confirmed from the cross-sectional photograph that the unevenness of the surface of the substrate is less

than 0.4 μm . Here, the smooth surface was formed over the entire surface of the substrate for the pellicle frame.

[0060] In the case when the anodization treatment is performed at each voltage, FIG. 6 shows SEM photographs of the surface of the substrate for the pellicle frame from which the anodic oxide film has been detached, the surface of the anodic oxide film, and a cross section of the anodic oxide film. Further, the thickness and detaching state of the anodic oxide film were also evaluated, and the results are shown together. When the voltage was 30 V, no spontaneous detachment of the anodic oxide film was observed.

[0061] It can be seen from FIG. 6 that there is a suitable voltage range for naturally detaching the anodic oxide film, and that the detachment can be promoted by applying a voltage of 40 to 50 V. Further, the thickness of the anodic oxide film also affects the spontaneous detachment phenomenon, and detachment can be promoted by making the thickness of the anodic oxide film 4 to 6 μm .

«Example 2»

[0062] Anodization treatment was carried out for 10 minutes at a voltage of 45 V in the same manner as in Example 1, except that cylindrical through holes having a diameter of 800 μm were provided in the thickness direction of the substrate for the pellicle frame.

[0063] FIG. 7 shows SEM photograph of the side surface of the through hole before anodization treatment and after detachment of the anodic oxide film. It can be seen that the surface from which the anodic oxide film was detached has been significantly smoothened compared to the surface before the anodization treatment.

«Example 3»

[0064] A rectangular bar of pure titanium of 40 mm $\times$ 4 mm $\times$ 1 mm was cut out, and a through hole having a diameter of 0.8 mm was drilled through the 40 mm $\times$ 1 mm surface to the back side. Next, the surface of the rectangular bar was physically polished to remove burrs, and then chemically polished by using a chemical polishing solution (TCP-08) at 30° C for 10 seconds. Next, in the same manner as in Example 1, the anodization treatment was carried out at a voltage of 45 V for 10 minutes.

[0065] The maximum height roughness (Rz) and the arithmetic mean roughness (Ra) of the 40 mm $\times$ 1 mm surface (front surface) and the inner surface of the through hole were measured before the anodization treatment (after chemical polishing) and after the anodization treatment (after detachment of the anodic oxide film). A white light interference microscope was used for the measurements. FIG. 8 shows a schematic diagram of the measurement lines on the 40 mm $\times$ 1 mm surface. The length of the measurement line in the longitudinal direction is 322 μm , and the length of the measurement line in the lateral direction is 244 μm . The measurement line on the inner surface of the through hole was 322 μm in the axial direction. Measurements were carried out in three regions in each of nine visual fields, and the average of a total of 27 measurements was calculated. The obtained results are shown in Table 1.

[Table 1]

	Surface (Longitudinal direction), μm		Surface (Lateral direction), μm		Inner wall of through hole, μm	
	Rz	Ra	Rz	Ra	Rz	Ra
Before anodization treatment	1.17	0.17	1.24	0.17	2.74	0.44
After anodization treatment	0.92	0.16	1.08	0.16	1.85	0.31

[0066] Both the maximum height roughness (Rz) and the arithmetic mean roughness (Ra) are reduced by the detachment of the anodic oxide film. It can be seen that the maximum height roughness (Rz) of the flat surface portions is all 1.1 μm or less, and the maximum height roughness (Rz) of the inner surface of the through hole is less than 2 μm . Further, after the anodization treatment, the arithmetic mean roughness (Ra) was less than 0.4 μm in all the measurement regions.

[0067] The surface conditions before the anodization treatment (after chemical polishing) and after the anodization treatment (after detachment of the anodic oxide film) were observed with a scanning electron microscope (SEM) and a microscope. FIG. 9 shows the microscopically observing images of the 40 mm $\times$ 1 mm surface, FIG. 10 shows the microscopically observing images of the inner surface of the through hole, and FIG. 11 shows the SEM image of the inner surface of the through hole. In every image, it can be seen that the surface is smoothened by the detachment of the anodic oxide film.

BRIEF EXPLANATION OF SYMBOLS

[0068]

- 5 1... Pellicle frame,
2... Through hole.

Claims

- 10 1. A surface-smoothened metal member comprising titanium or a titanium alloy, **characterized in that:**
- a maximum length of the metal member is 50 to 1000 mm;
a maximum height roughness (Rz) of a flat surface portion of the metal member is 1.1 μm or less; and
a maximum height roughness (Rz) of a portion of the surface of the metal member having a radius of curvature of
15 0.05 to 2.5 mm is less than 2 μm .
2. The surface-smoothened metal member according to claim 1, wherein
- the metal member has a through hole and/or an opening, and
20 a maximum height roughness (Rz) of an inner wall of the through hole and/or opening is also less than 2 μm .
3. A surface-smoothened metal member comprising titanium or a titanium alloy, **characterized in that**
- a maximum length of the metal member is 50 to 1000 mm;
25 an arithmetic mean roughness (Ra) of a portion of the surface of the metal member having a radius of curvature of
0.05 to 2.5 mm is less than 0.4 μm .
4. The surface-smoothened metal member according to claim 3, wherein
- 30 the surface-smoothened metal member of the present invention has a through hole and/or an opening in the metal
member, and
the arithmetic mean roughness (Ra) of the inner wall of the through hole and/or the opening is also less than 0.4
 μm .
- 35 5. The surface-smoothened metal member according to claim 2 or 4, wherein
an equivalent circle diameter of the through hole and/or the opening is 0.1 to 5 mm.
6. The surface-smoothened metal member according to claim 2 or 4, wherein
a depth of the through hole and/or the opening is 1 to 50 mm.
40
7. The surface-smoothened metal member according to any one of claims 1 to 6, wherein
the metal member is a frame body.
8. A method for manufacturing a surface-smoothened metal member, comprising:
45
- subjecting a substrate made of titanium or a titanium alloy to anodization treatment to form an anodic oxide film on
the surface of the substrate; and
smoothing the surface of the substrate by detaching the anodic oxide film.
- 50 9. The method for manufacturing a surface-smoothened metal member according to claim 8, wherein a thickness of the
anodic oxide film is set to 2 to 10 μm .
10. The method for manufacturing a surface-smoothened metal member according to claim 8 or 9, wherein an applied
voltage in the anodization treatment is set to 20 to 100 V
55
11. The method for manufacturing a surface-smoothened metal member according to any one of claims 8 to 10, wherein
the formation and detachment of the anodic oxide coating is repeated until an arithmetic mean roughness (Ra) of less
than 0.4 μm and/or a maximum height roughness (Rz) of less than 2 μm is obtained on the surface of the substrate.

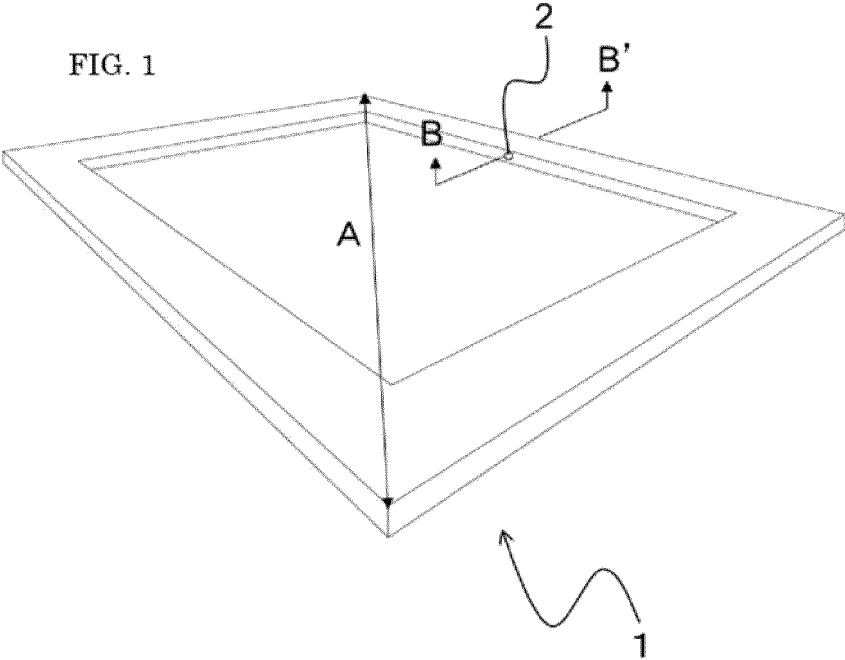


FIG. 2

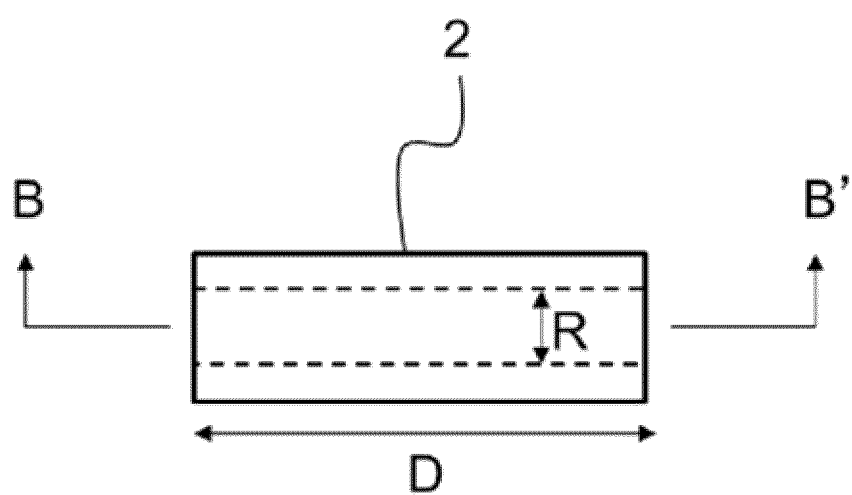


FIG. 3

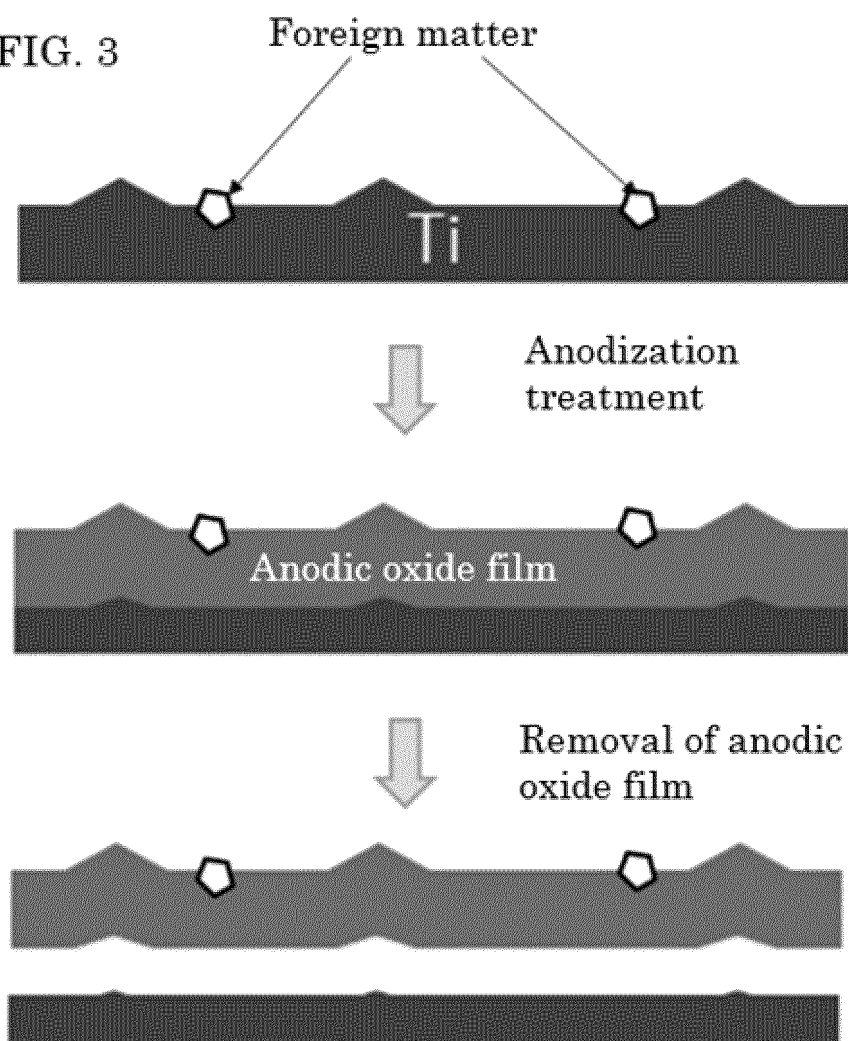


FIG. 4

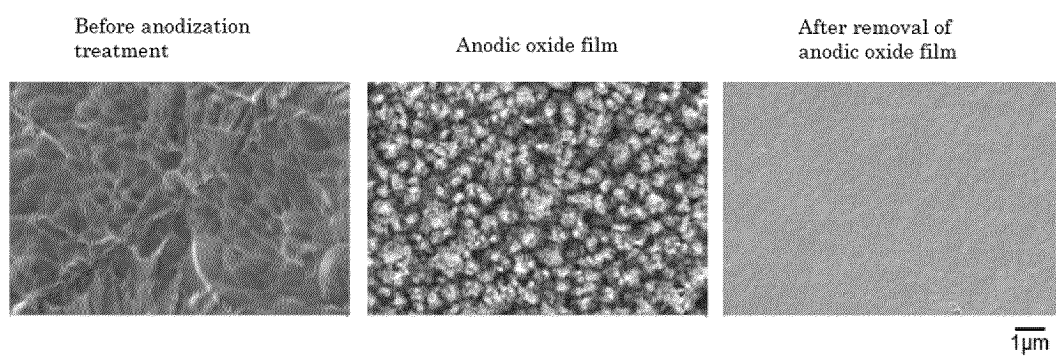


FIG. 5

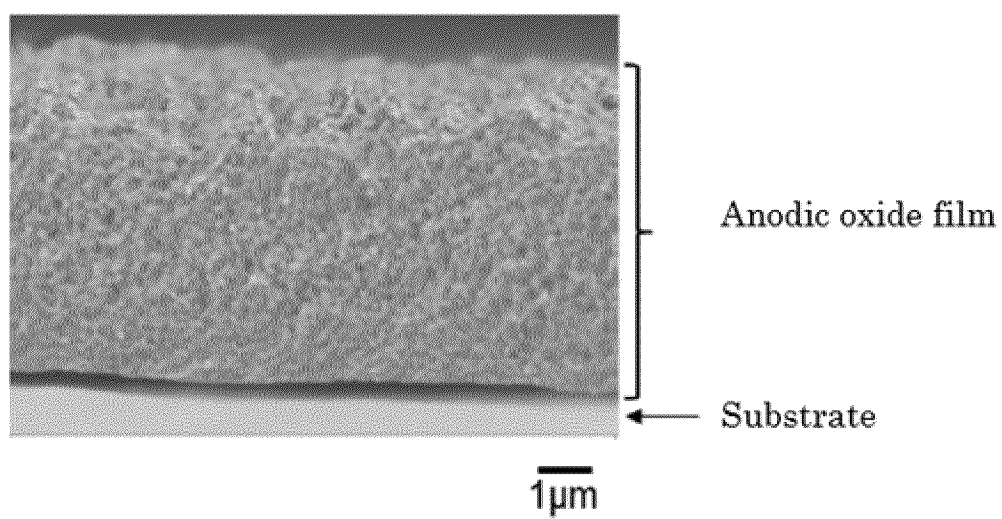


FIG. 6

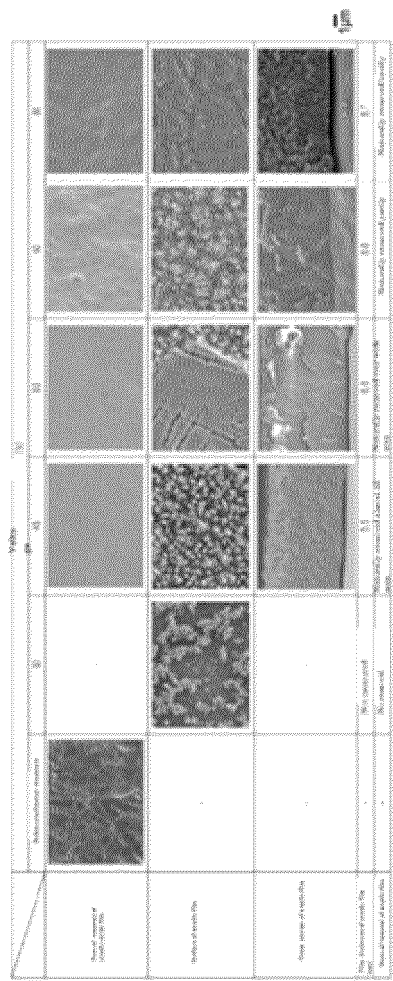


FIG. 7

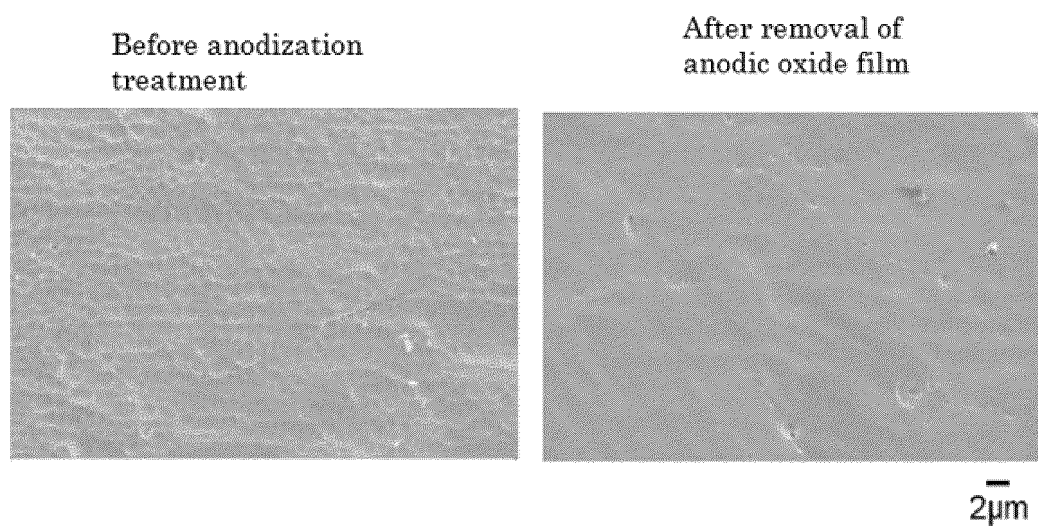


FIG. 8

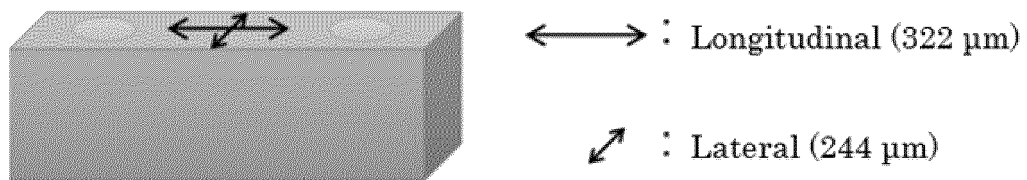
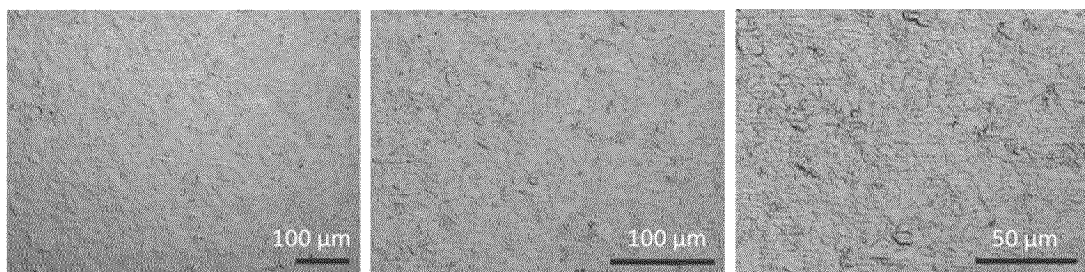


FIG. 9

Before anodization treatment



After anodization treatment

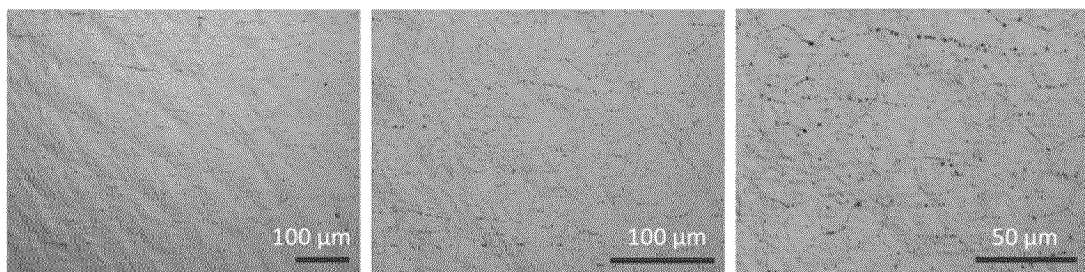
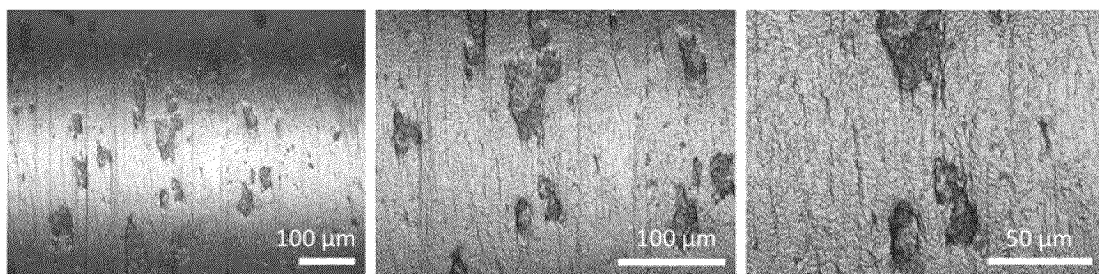


FIG. 10

Before anodization treatment



After anodization treatment

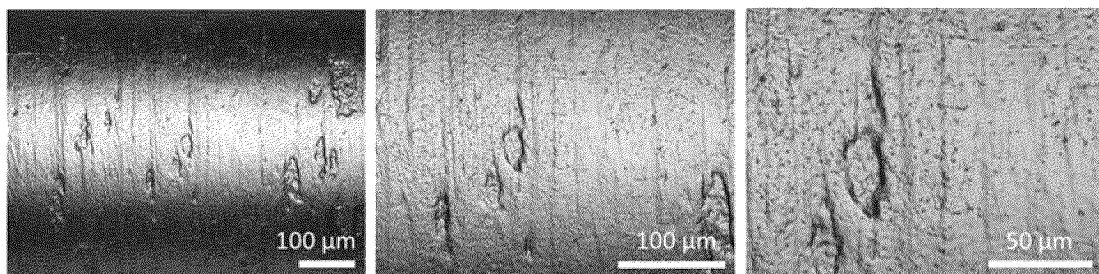
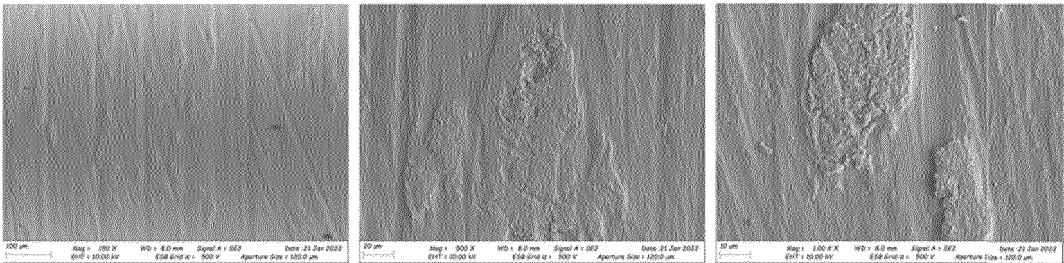
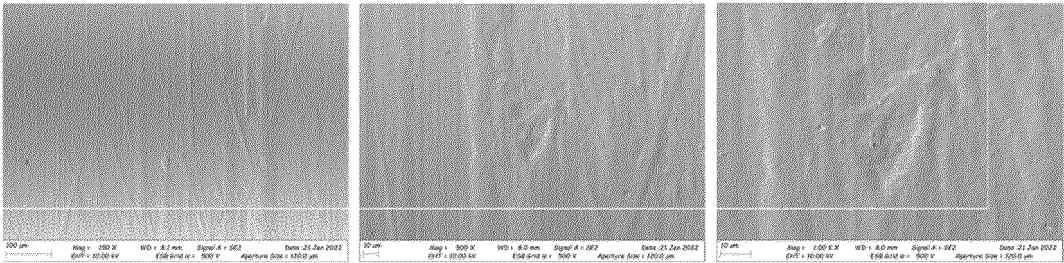


FIG. 11

Before anodization treatment



After anodization treatment



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/043140

A. CLASSIFICATION OF SUBJECT MATTER**C25D 11/26**(2006.01)i

FI: C25D11/26 302

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)

C25D11/26

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

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

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

JSTPlus/JST7580 (JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2008-223139 A (POLIGRAT GMBH) 25 September 2008 (2008-09-25) claims, paragraphs [0002], [0003]	1-7
A		8-11
Y	JP 2004-043850 A (MITSUBISHI GAS CHEM CO INC) 12 February 2004 (2004-02-12) claims, paragraph [0001], table 1	1-7
A		8-11
Y	JP 2006-299388 A (NIPPON OIL CORP) 02 November 2006 (2006-11-02) claims, paragraph [0011]	1-7
A		8-11
A	JP 2019-039060 A (NIPPON LIGHT METAL CO) 14 March 2019 (2019-03-14) claims	1-11

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

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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 February 2023

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Name and mailing address of the ISA/JP

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Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/043140

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JP 2019-039060 A	14 March 2019	WO 2019/044368 A1 claims TW 201912813 A KR 10-2020-0036042 A CN 111051577 A	

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REFERENCES CITED IN THE DESCRIPTION

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