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(54) **Ceramics for decorative component and decorative component for watch using the same**

(57) To provide ceramics for decorative component, which give high-grade impression, aesthetic satisfaction and mind soothing effect with golden color tone which is popular in the marketplace, and a decorative component for a watch that uses the same.

The ceramics for decorative component comprise titanium nitride as a main component, nickel as the auxiliary component, and at least one kind selected from among a group of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten

carbide and tantalum carbide as an additional component, wherein the arithmetic mean height Ra of at least the decorative surface is 0.03 μm or less, and the decorative surface has such a color tone that lightness index L* is in a range from 72 to 84, and chromaticness indices a* and b* are from 4 to 9 and 28 to 36, respectively, in the L*a*b* color space of CIE1976. This constitution increases the reflectivity of the decorative surface to light, and improves the luster of the color tone, thus achieving high-grade impression and aesthetic satisfaction.

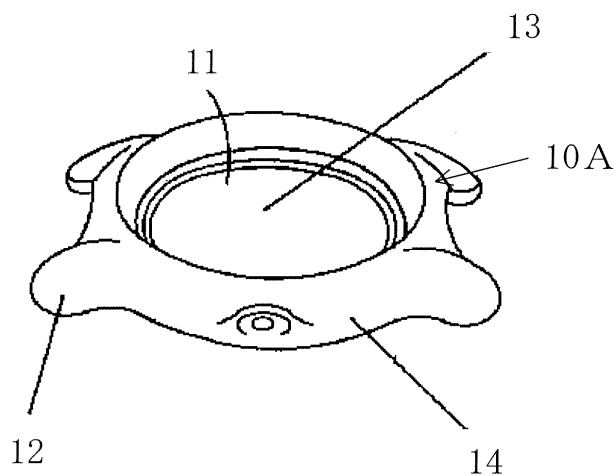


Fig. 1 (a)

Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to ceramics for decorative component used in decorative components of accessory, decorative components for watch, decorative architectural members, decorative components for kitchen utensil, etc. and, more particularly, to decorative components for watch used in the case of wrist watch links of watchband, etc. so as to provide beautiful color.

10 BACKGROUND ART

[0002] Decorative components for watch and decorative components for accessory having golden color have been made from gold or an alloy thereof, or by plating various metals, for the reason of color tone and corrosion resistance.

15 **[0003]** An example of plated metal is a product having golden mirror-finished surface disclosed in Japanese Examined Patent Publication (Kokoku) No. 7-62274, which is made by coating the surface of a metal with an alloy plating comprising Cu, Zn and Ni in proportions of 70 to 85:15 to 25:1 to 10 in terms of atomic % of elements precipitated, wherein the coating film has a color tone in a range of $L^* = 80$ to 95 , $a^* = -5$ to 0 and $b^* = 15$ to 25 in the $L^*a^*b^*$ color space of CIE1976.

[0004] However, gold, alloy of gold and plated metallic material are low in hardness, and therefore have such a problem that the surface can be damaged such as scratch or deformation through contact with a hard object.

20 **[0005]** Recently, various ceramics for decorative components have been proposed to solve this problem.

[0006] Japanese Examined Patent Publication (Kokoku) No. 4-47020 and Japanese Examined Patent Publication (Kokoku) No. 4-47021, for example, propose ceramics for decorative component, which maintain golden color tone by means of a hard phase composed mainly of TiN_z ($0.6 \leq Z \leq 0.95$). It is shown that the color tone shifts from golden color tone to pale golden color as the value of Z becomes lower than the value dictated by the stoichiometrical composition, and that the color tone can be easily controlled in a range from deep and pale golden color to sharp golden color, by adding TiO , ZrN , HfN , VN , NbN , TaN , CrN , Cr_2N , TaC , NbC .

25 **[0007]** Japanese Unexamined Patent Publication (Kokai) No. 2003-13154 discloses ceramics for decorative component, which contain 45 to 75% by weight of titanium nitride and 7.5 to 25% by weight of titanium carbide as the hard phase, 1 to 10% by weight of chromium in terms of equivalent carbide, 0.1 to 5% by weight of molybdenum in terms of equivalent carbide and 5 to 20% by weight of nickel as the binder phase, and has lightness index L^* from 65 to 69, chromaticness indices a^* and b^* from 4 to 9 and from 5 to 16, respectively, in the $L^*a^*b^*$ color space of CIE1976.

DISCLOSURE OF THE INVENTION

35 **[0008]** However, even when the products having golden mirror-finished surface proposed in Japanese Examined Patent Publication (Kokoku) No. 7-62274 is used as a decorative component, the problem that the coating film peels off cannot be avoided since the golden color tone is provided by coating a metal with an alloy plating of copper, zinc and nickel.

[0009] Japanese Examined Patent Publication (Kokoku) No. 4-47020 and Japanese Examined Patent Publication (Kokoku) No. 4-47021 show that the color tone can be easily controlled in a range from deep and pale golden color to sharp golden color by adding TiO , ZrN , HfN , VN , NbN , TaN , CrN , Cr_2N , TaC and NbC . However, there are no descriptions on specific method of control and quantitative account of the color tone of the ceramics for decorative component, thus providing no hint on how to control the color tone.

[0010] The ceramics for decorative component disclosed in Japanese Unexamined Patent Publication (Kokai) No. 2003-13154 are composed of a sintered material, and therefore does not have the problem of peel-off and demonstrates high corrosion resistance, but its color is a combination of silver, violet and pink, not golden color tone.

40 **[0011]** The ceramics for decorative component of the present invention comprise titanium nitride as a main component, nickel as an auxiliary component, and at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as an additional component, wherein at least arithmetic mean height R_a of the decorative surface is $0.03 \mu m$ or less, and the decorative surface has such a color tone that lightness index L^* is in a range from 72 to 84, and chromaticness indices a^* and b^* are from 4 to 9 and 28 to 36, respectively, in the $L^*a^*b^*$ color space of CIE1976.

[0012] The present invention is also characterized in that the titanium nitride has a composition formula of TiN_x ($0.8 \leq x \leq 0.96$).

[0013] The present invention is also characterized by further containing chromium as the additional component.

55 **[0014]** The present invention is further characterized by containing 7% or more and not more than 14.5% by weight of nickel as the auxiliary component, 2.5% or more and not more than 10% by weight of at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide and 1.5% or more and not more than 6.5% by weight of chromium are contained as the additional components.

[0015] The present invention is further characterized by containing 1.5% or more and not more than 6.5% by weight of chromium.

[0016] The present invention is further characterized by the fact that the additional component is at least one of niobium carbide, molybdenum carbide, tungsten carbide and tantalum carbide, of which content is 3% or more and not more than 8% by weight.

[0017] The present invention is further characterized by the fact that a void ratio in the decorative surface is 3% or less.

[0018] The decorative component for watch of the present invention is characterized by being made of the ceramics for decorative component of the present invention having the constitution described above.

EFFECTS OF THE INVENTION

[0019] The ceramics for decorative component of the present invention comprises titanium nitride as a main component, nickel as an auxiliary component, and at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as an additional component, wherein at least arithmetic mean height R_a of the decorative surface is $0.03\ \mu\text{m}$ or less, and the decorative surface has such a color tone that lightness index L^* is in a range from 72 to 84, chromaticness indices a^* and b^* are from 4 to 9 and from 28 to 36, respectively, in the $L^*a^*b^*$ color space of CIE1976 so that the decorative surface has high reflectivity to light and lustrous color tone, and provides high-grade impression and aesthetic satisfaction.

[0020] In the ceramics for decorative component of the present invention, since the titanium nitride has a composition formula of TiN_x ($0.8 \leq x \leq 0.96$) of non-stoichiometrical composition, the lightness index L^* can be increased so that the decorative surface has high reflectivity to light and lustrous color tone, and provides high-grade impression and aesthetic satisfaction.

[0021] The ceramics for decorative component of the present invention also contain chromium as the additional component, and therefore have improved corrosion resistance, so as to be capable of maintaining high-grade impression, aesthetic satisfaction and mind soothing effect over an extended period of time.

[0022] The ceramics for decorative component of the present invention also contain 7% or more and not more than 14.5% by weight of nickel as the auxiliary component, and 2.5% or more and not more than 10% by weight of at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as the additional components, and the proportion of the auxiliary component is optimized so as to increase the reflectivity of the decorative surface to light.

[0023] The ceramics for decorative component of the present invention further contain 1.5% or more and not more than 6.5% by weight of chromium, and therefore can demonstrate corrosion resistance and clearness of color tone at the same time.

[0024] The ceramics for decorative component of the present invention further includes at least one of niobium carbide, molybdenum carbide, tantalum carbide and tungsten carbide as the additional component, of which concentration is 3% or more and not more than 8% by weight. Since these the additional components act to suppress the crystal grains from growing, crystal boundaries grow and the incident light is subjected to mirror reflection on the crystal that forms the decorative surface and diffusive reflection on the crystal boundaries. Lightness index L^* and chromaticness index b^* of the decorative surface can be made higher and enhanced effect of improving the color tone can be achieved, so that lustrous color tone can be enhanced and high-grade impression and aesthetic satisfaction can be obtained.

[0025] Also because the decorative surface of the ceramics for decorative component of the present invention has a void ratio of 3% or less, surface unevenness can be decreased for the decorative surface. As a result, the value of lightness index L^* can be increased and therefore higher luster and higher aesthetic satisfaction can be achieved.

[0026] Moreover, because the ceramics for decorative component of the present invention have high-grade impression and aesthetic satisfaction and provides mind soothing effect through visual sense, they can be preferably used as decorative component for watch for a time piece which is required to provide proper function and aesthetic satisfaction while being worn or kept near the user.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027]

Fig. 1 (a) is a perspective view on the front surface of the watch case in an example of a watch case that is the decorative component for watch of the present invention, and

Fig. 1 (b) is a perspective view on the back surface of the watch case shown in Fig. 1 (a).

Fig. 2 is a perspective view showing another example of watch case as an application of the decorative component for watch of the present invention.

Fig. 3 is a schematic view showing an example of constitution of watchband as an application of the decorative

component for watch of the present invention.

[Description of Reference Numerals]

5 **[0028]**

10A, 10B: Watch case

11: Recess

10 12: Projection

13: Bottom

15 14: Wall

15: Hole

20: Inner link

20 21: Through hole

30: Outer link

25 31: Pin hole

40: Pin

50: Watchband

30

BEST MODE FOR CARRYING OUT THE INVENTION

[0029] Preferred embodiments of the present invention will now be described.

35 **[0030]** The ceramics for decorative component of the present invention comprise titanium nitride as a main component, nickel as an auxiliary component, and at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as an additional component.

40 **[0031]** The main component in the present invention refers to a component that occupies 50% by weight or more of the composition of the ceramics for decorative component. The auxiliary component in the present invention refers to a component that occupies less than 50% by weight of the composition of the ceramics for decorative component. The auxiliary component and the additional component in the present invention may occupy the same proportions of the composition by weight.

[0032] Titanium nitride contained as the main component provides golden color which is favorable for a decorative component, and also provides favorable mechanical properties such as strength and hardness. In order to obtain such a golden color, it is preferable to include 70% by weight or more titanium nitride.

45 **[0033]** Nickel contained as the auxiliary component serves as a binder that bonds the crystals of titanium nitride contained as the main component and the additional component.

50 **[0034]** Moreover, at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide contained as the additional component serves as a color tone control agent. Vanadium nitride, niobium nitride and tantalum nitride form solid solution with titanium nitride, while niobium carbide, tungsten carbide and tantalum carbide exist in molten form in nickel.

[0035] In the ceramics for decorative component of the present invention, at least arithmetic mean height Ra of the decorative surface is 0.03 μm or less, and the decorative surface has such a color tone that lightness index L* is not less than 72 and not more than 84, and chromaticness indices a* and b* are respectively not less than 4 and not more than 9, and not less than 28 and not more than 36 in the L*a*b* color space of CIE1976.

55 **[0036]** This constitution provides the owner who seeks decorative value with high-grade impression, aesthetic satisfaction, mind soothing effect, and also shows golden color tone. Since arithmetic mean height Ra of the decorative surface affects the reflectivity thereof to light and the reflectivity is increased by setting the arithmetic mean height Ra to 0.03 μm or less, the value of lightness index L* can be increased. When the arithmetic mean height Ra of the decorative

surface is larger than $0.03\text{ }\mu\text{m}$, the value of lightness index L^* decreases thus resulting in darker color and high-grade feeling is compromised. The reason why the arithmetic mean height R_a of the decorative surface is set to $0.03\text{ }\mu\text{m}$ or less is that a larger value of arithmetic mean height R_a of the decorative surface affects reflectivity of the decorative surface to light and causes the color tone to vary.

[0037] The light mentioned above is a collection of visible light components having wavelengths ranging from 380 to 780 nm. By setting the arithmetic mean height R_a of the decorative surface to $0.03\text{ }\mu\text{m}$ or less, the visible light is broken into components of different wavelengths. As reflection of light in a region of wavelengths from 450 to 500 nm which corresponds to blue color is suppressed and reflection of light in a region of wavelengths from 570 to 590 nm which corresponds to yellow color is increased, golden color is obtained by setting the arithmetic mean height R_a to $0.03\text{ }\mu\text{m}$ or less.

[0038] Particularly, the reflectivity of the decorative surface to light in a region of wavelengths from 570 to 700 nm is preferably 50% or more.

[0039] The arithmetic mean height R_a may be measured in accordance to JIS B 0601-2001. When measuring with a touch probe type surface roughness meter with the measurement length and the cut-off point being set to 5 mm and 0.8 mm, respectively, for example, a stylus having tip radius of $2\text{ }\mu\text{m}$ may be put into contact with the decorative surface of the ceramics for decorative component having disk shape of diameter from 10 to 20 mm, and scanned at a speed of 0.5 mm/sec. The arithmetic mean height R_a of the decorative surface is the mean value of arithmetic mean heights R_a of the decorative surface measured at 5 points.

[0040] When the value of lightness index L^* is in a range from 72 to 84, and the values of chromaticness indices a^* and b^* are set in ranges from 4 to 9 and from 28 to 36 in the $L^*a^*b^*$ color space of CIE1976 in the manufacturing method to be described later with the composition of the ceramics for decorative component set as described above, it is made possible to achieve enhanced effect of improving the color tone. Therefore, high-grade impression and aesthetic satisfaction are provided. As a result, mind soothing effect is obtained through visual sense.

[0041] The lightness index L^* indicates the degree of lightness or darkness of a color tone, while a higher value of the lightness index L^* means lighter color tone and a lower value of the lightness index L^* means darker color tone. The value of lightness index L^* is set in a range from 72 to 84, because the golden color tone has satisfactory lightness in this range. When this value is lower than 72, the color tone becomes darker with plain impression and when this value is higher than 84, the color tone becomes too light without high-grade impression, in either case high-grade impression and aesthetic satisfaction cannot be obtained. The lightness index L^* is more preferably not less than 72 and not more than 79.

[0042] The chromaticness index a^* represents the position in red to green axis of color tone. A larger positive value of chromaticness index a^* means red color, and a smaller absolute value of chromaticness index a^* means dull color tone without clearness, while a negative chromaticness index a^* having a larger absolute value means green color. Value of chromaticness index a^* is set in a range from 4 to 9, since reddish color can be suppressed without compromising the sharpness of the color tone. When the value of chromaticness index a^* is less than 4, the color tone becomes dull and an attempt to obtain a sharp color tone results in green color. When the value of chromaticness index a^* is more than 9, the color tone becomes increasingly reddish with flashy impression, losing high-grade impression.

[0043] The chromaticness index b^* represents the position in yellow to blue axis of color tone. A larger positive value of chromaticness index b^* means yellow color tone, and a smaller absolute value of chromaticness index b^* means dull color tone without clearness, while a negative chromaticness index b^* having a larger absolute value means blue color. Value of chromaticness index b^* is set in a range from 28 to 36, since golden color tone can be obtained without compromising the sharpness of the color tone in this range. When the value of chromaticness index b^* is less than 28, the color tone becomes dull. When the value of chromaticness index b^* is more than 36, the color tone becomes increasingly yellowish, thus losing golden color tone and high-grade impression. As a result, satisfaction and mind soothing effect cannot be obtained.

[0044] In the present invention, the decorative surface of the ceramics for decorative component refers only to a surface of a decorative component which is required to have decorative value. In case the ceramics for decorative component of the present invention are used for a watch case, the outside surface of the watch case is subjected to aesthetic evaluation and is required to have decorative value, and is therefore a decorative surface.

[0045] The values of lightness index L^* and the chromaticness indices a^* and b^* in the $L^*a^*b^*$ color space of CIE1976 can be measured by the procedure specified in JIS Z 8722-2000. For example, a spectrophotometer (CM-3700d from Konica Minolta Holdings Inc., etc.) may be used in combination with CIE standard light source of D65 with view angle being set to 10 degrees and the measurement area set to 5 mm by 7 mm.

[0046] Color tone of the ceramics for decorative component of the present invention is affected by the number of atoms x in the formula TiN_x . As the number of atoms x becomes smaller, the color tone changes from golden color to pale golden color. As the number of atoms x becomes larger, the color tone changes to dark golden color like Buddhist altar. Accordingly, the number of atoms x in the formula TiN_x is preferably 0.8 or larger and not larger than 0.96. Titanium nitride can change to titanium carbonitrideoxide (TiCN_xO) when degreased or fired through substitution or reaction with

oxygen and carbon included in the atmosphere. The number of atoms x can be determined by means of an oxygen-nitrogen analyzer and a carbon analyzer. Specifically, after measuring the proportions of oxygen, nitrogen and carbon to titanium nitride in terms of 100% by weight with these analyzers, the total content of these elements is subtracted from the amount of titanium nitride in 100% by weight, and the remainder is divided by the atomic weight 47.9 of titanium, thereby to obtain the number of titanium atoms included in TiN_x . The number of nitrogen atoms in TiN_x can be determined by dividing the proportion of nitrogen by the atomic weight 14 of nitrogen. Number of nitrogen atoms when the number of titanium atoms is assumed to be 1 is the number of atoms x .

[0047] The ceramics for decorative component of the present invention preferably further contain chromium as the additional component. Chromium is capable of bonding with oxygen contained in the air so as to form a dense oxide film on the decorative surface, thereby improving corrosive resistance and maintaining high-grade impression, aesthetic satisfaction and mind soothing effect over an extended period of time.

[0048] It is particularly preferable that the ceramics for decorative component of the present invention contain not less than 7% and not more than 14.5% by weight of nickel as the auxiliary component, and not less than 2.5% by weight and not more than 10% by weight of at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as the additional component.

[0049] The content of nickel is set in a range from 7% to 14.5% by weight, because it is preferable to include much nickel content which serves as a binder that bonds the crystal of the auxiliary component and the crystal of titanium nitride, although an excessive content of nickel in the ceramics for decorative component may induce nickel dissolving when the ceramic for decorative component are put into contact with human skin. When the nickel content is less than 7% by weight, crystal of the auxiliary component and crystal of titanium nitride cannot be sufficiently bonded together, and the ceramics for decorative component cannot be made dense enough, thus resulting in a low strength. When the nickel content is more than 14.5% by weight, nickel dissolving may be induced in the human body on which the ceramics for decorative component are worn. In case the ceramics for decorative component are used in goods which are worn on the human body such as the case of a wrist watch or links of a watchband, in particular, the nickel content is more preferably in a range from 7% to 9% by weight. It is also preferable to include 2% by weight or less chromium which has the effect of preventing nickel from eluting, in order to prevent nickel dissolving from being contained by the elution of nickel.

[0050] The reason why the content of the additional component is set in a range not less than 2.5% and not more than 10% by weight is that nitrides such as vanadium nitride, niobium nitride, tantalum nitride among the additive components have the functions to control the color tone, such that the value of chromaticness index b^* can be increased as the nitride described above forms solid solution with titanium nitride, while the content of the additional component less than 2.5% by weight leads to smaller amount of solid solution with titanium nitride which may make it impossible to obtain chromaticness index b^* of 30 or higher, and the content of the additional component more than 10% by weight makes it difficult to sinter the nitrides since they have high tendency of forming covalent bond.

[0051] Moreover, it is preferable to contain, among the nitrides, vanadium nitride in the amount of not less than 2.5% by weight and not more than 6% by weight, since vanadium nitride of a proportion in this range can easily form solid solution.

[0052] While carbides such as molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide function as a color control agent similarly to nitrides, but do not form solid solution with titanium nitride unlike the nitrides and, instead, melts inside of nickel, thereby to increase the value of chromaticness index b^* . When the carbide content is less than 2.5% by weight, the amount thereof taken into the inside of nickel becomes smaller and it may become impossible to achieve chromaticness index b^* of 30 or higher. When the carbide content is more than 10% by weight, it becomes difficult to sinter the carbide since they have high tendency of forming covalent bond.

[0053] Corrosion resistance and clearness of color of the ceramics for decorative component of the present invention are affected by the content of chromium. When a high chromium content is included, corrosion resistance becomes higher but the values of chromaticness indices a^* and b^* become lower. When the chromium content is low, corrosion resistance becomes lower but the values of chromaticness indices a^* and b^* become higher. The ceramics for decorative component of the present invention preferably contain 1.5% or more and not more than 6.5% by weight of chromium, since both corrosion resistance and clearness can be achieved at the same time in this range.

[0054] The content of carbides such as molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide is more preferably 3% or more and not more than 8% by weight.

[0055] This is because, since these additional components act to suppress crystal grains from growing, crystal boundaries grow and the incident light is significantly influenced also by diffusive reflection on the crystal boundaries as well as by mirror reflection on the crystal that forms the decorative surface. Due to this influence, values of lightness index L^* and chromaticness index b^* of the decorative surface become higher, so as to achieve enhanced effect of improving the color tone. Therefore, high-grade impression and aesthetic satisfaction are obtained with color tone of higher luster. As a result, mind soothing effect is obtained through visual sense.

[0056] Light can be reflected by either mirror reflection or diffusive reflection. Mirror reflection in the present invention refers to reflection that occurs with reflection angle equal to the incident angle after entering the decorative surface which

is finished like a mirror, or hitting the crystal that forms the decorative surface. Diffusive reflection refers to the behavior of light entering the crystal boundaries and exiting therefrom after repetitive random reflections.

[0057] The surface roughness of the crystal constituting the decorative surface can be controlled by barrel polishing described hereinafter and the surface roughness of the crystal face when measured by an atomic force microscope is preferably controlled in a range from 1 to 2 nm in terms of the arithmetic mean height Ra. In the above range, there is a tendency that reflection on the crystal face partially varies from mirror reflection to diffusive reflection, and chromaticness index b* of the decorative surface can be controlled to 32 or more.

[0058] It is preferable to contain at least one of vanadium nitride, niobium nitride and tantalum nitride and at least one of molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as the additional component. Thus both the action of increasing the values of chromaticness index b* as the nitrides form solid solution with titanium nitride, and the action of increasing the values of the lightness index L* and chromaticness index b* as the carbides melt in nickel can be achieved.

[0059] In the ceramics for decorative component of the present invention, nickel as the auxiliary component surrounds chromium, which is the additional component, and forms grain boundary phase that binds titanium nitride so that nickel and chromium react with each other to form nickel chromium compound. As a result, ionization and elution of nickel does not occur, thus making it possible to improve the mechanical properties and the corrosion resistance.

[0060] The state that nickel as the auxiliary component surrounds chromium which is the additional component means such a state that chromium is surrounded by the grain boundary phase without making contact with the crystal of titanium nitride.

[0061] The state that nickel surrounds chromium can be checked by comparing an image of the decorative surface taken with a scanning electron microscope and an image of the decorative surface showing the distributions of nickel and chromium which are detected by energy dispersion type (EDS) X-ray microanalyser.

[0062] It is preferable that the decorative surface of the ceramics for decorative component of the present invention has a void ratio of 3% or less. Voids in the decorative surface exert influence particularly on the value of lightness index L*. When there are much voids, the value of lightness index L* decreases. When there are less voids, the value of lightness index L* increases. By controlling the void ratio in the decorative surface to 3% or less, it is made possible to control the lightness index L* within a range from 75 to 79, thus resulting in color tone that is more loved by people. It is more preferable to control the lightness index L* within a range from 77 to 79, in which case it is preferable to control the void ratio to 2% or less.

[0063] The void ratio in the decorative surface may be determined by capturing an image of the decorative surface with a CCD camera under a metallurgical microscope with a magnifying power of 200 times, and measuring at 20 points in one field of view, with the measuring area of one field of view in the image being set to $2.25 \times 10^{-2} \text{ mm}^2$, number of fields of view set to 20 and total measuring area to $4.5 \times 10^{-1} \text{ mm}^2$, by using an image analyzer (LUZEX-FS, manufactured by NIRECO Corporation).

[0064] The decorative component for watch of the present invention is made of the ceramics for decorative component of the present invention having the constitution described above, such as a watch case or links of a watchband. Fig. 1 shows an example of a watch case as an application of the decorative component for watch made of the ceramics for decorative component of the present invention, where Fig. 1 (a) is a perspective view on the front surface of the watch case, and Fig. 1 (b) is a perspective view on the back surface of the watch case. Fig. 2 is a perspective view showing another example of watch case as an application of the decorative component for watch of the present invention.

Fig. 3 is a schematic view showing an example of the constitution of watch case as an application of the decorative component for watch of the present invention. In these drawings, identical parts are given the same reference numerals.

[0065] The watch case 10A shown in Fig. 1 has a recess 11 which accommodates a movement (drive mechanism) which is not shown, and protrusions 12 which engage a watchband (not shown) for wearing the watch on a wrist, where the recess 11 is composed of a thin bottom 13 and a thick wall 14. The watch case 10B shown in Fig. 2 has a recess 15 which accommodates a movement (drive mechanism) which is not shown, and protrusions 12 which engage a watchband (not shown) for wearing the watch on a wrist provided on the wall 14.

[0066] The links that constitute the watchband 50 shown in Fig. 3 include inner links 20 each having a through hole 21 penetrated by a pin 40 and outer links 30 each having pin hole 31 in which an end of the pin 40 is inserted. The inner links 20 and the outer links 30 are linked with each other by inserting the ends of the pin 40 which penetrates the through hole 21 of the inner link 20 into the pin holes 31 of the outer links 30, thereby to assemble the watchband 50.

[0067] The watch cases 10A, 10B and the links that constitute the watchband 50 are made of the ceramics for decorative component of the present invention, and use thereof makes it possible to provide high-grade impression, aesthetic satisfaction to the watch and mind soothing effect obtained through visual sense.

[0068] The ceramics for decorative component of the present invention preferably have Vickers hardness (Hv) of 8 GPa or higher, since the level of Vickers hardness (Hv) of the decorative surface is one of factors that affect the long-term stability. With such a level of Vickers hardness (Hv), the decorative surface is less likely to be mechanically impaired even when put into contact with hard substances such as glass or metallic particles. Vickers hardness (Hv) of the

decorative surface may be measured according to JIS R 1610-2003.

[0069] Rupture toughness which affects the wear resistance of the decorative surface is preferably as high as possible. In the ceramics for decorative component of the present invention, rupture toughness is preferably $4 \text{ MPa}\cdot\sqrt{\text{m}}$ or higher. Rupture toughness can be measured by injection filler method (IF method) specified in JIS R 1607-1995. Ceramics for decorative component which is worn on a human body is desired to be lighter in weight. Therefore, apparent density of the ceramics for decorative component of the present invention is preferably not higher than 6 (higher than 0). Apparent density can be measured according to JIS R 1634-1998. In case the ceramics for decorative component constitutes the inner links 20 which are part of the links of a watchband, the inner links 20 are frequently subjected to tensile load. In the ceramics for decorative component of the present invention, tensile strength of the links is preferably 196 N or higher. The tensile strength can be determined by, with a pin (not shown) made of hard metal which is longer than the length of the through hole 21 inserted in the through holes 21a, 21b of the inner link 20, pulling the pin in a direction to depart and reading the strength of the inner link 20 at rupture with a load cell. In case the ceramics for decorative component constitutes a watch case or inner links of a watchband, total content of ferromagnetic metals such as cobalt (Co) having mass susceptibility of $162 \text{ G}\cdot\text{cm}^3/\text{g}$ or higher included in the ceramics for decorative component is preferably 0.1% by weight or less, when the adverse effect on the movement (drive mechanism) (not shown) which is not shown is taken into consideration. The proportion of the ferromagnetic metal can be measured by ICP (inductivity coupled plasma) emission spectrometry.

[0070] A method for manufacturing ceramics for decorative component of the present invention will now be described.

[0071] To manufacture the ceramics for decorative component of the present invention, first a stock material powder is prepared by weighing and mixing a predetermined amount of titanium nitride, nickel, and at least one of vanadium nitride, niobium nitride and tantalum nitride powders. More specifically, a titanium nitride powder having a mean particle size of 10 to $30 \mu\text{m}$, a nickel powder having a mean particle size of 10 to $20 \mu\text{m}$, and at least one of a vanadium nitride powder, a niobium nitride powder and a tantalum nitride powder having a mean particle size of 2 to $10 \mu\text{m}$ are prepared, crushed and mixed in such a composition containing 76 to 90.5% by weight of a titanium nitride powder, 7 to 14.5% by weight of a nickel powder, and 2.5 to 10% by weight of a nitride powder.

[0072] When particularly high corrosion resistance is required, the materials may be weighed, crushed and mixed in such a composition containing 77.0 to 83.5% by weight of a titanium nitride powder, 10.0 to 13.0% by weight of a nickel powder, 4.0 to 8.0% by weight of a nitride powder and 1.5 to 6.5% by weight of a chromium powder.

[0073] In order to form the grain boundary phase that binds titanium nitride with nickel surrounding chromium that is the additional component, it is necessary to increase the possibility of the nickel powder and the chromium powder making contact with each other. The possibility may be increased by making the duration of crushing and mixing process longer, for example to 150 hours or more.

[0074] While the manufacturing method described above involves the use of nitride as the additive component, at least one of molybdenum, niobium, tungsten and tantalum, instead of the nitride, may be mixed with the titanium nitride powder and the nickel powder. More specifically, a titanium nitride powder having a mean particle size of 10 to $30 \mu\text{m}$, a nickel powder having a mean particle size of 10 to $20 \mu\text{m}$, and at least one of molybdenum, niobium, tungsten and tantalum powders having a mean particle size of 1 to $50 \mu\text{m}$ are prepared, crushed and mixed in such a composition containing 75.5 to 92% by weight of a titanium nitride powder, 7 to 14.5% by weight of a nickel powder, and 1 to 10% by weight of a metal powder.

[0075] When particularly high corrosion resistance is required, the materials may be weighed, crushed and mixed in such a composition containing 77.0 to 83.5% by weight of a titanium nitride powder, 10.0 to 13.0% by weight of a nickel powder, 4.0 to 8.0% by weight of a metal powder and 1.5 to 6.5% by weight of a chromium powder.

[0076] In order to form the grain boundary phase that binds titanium nitride in such a state as nickel surrounds chromium that is the additional component, duration of crushing and mixing process may be set to 150 hours or more.

[0077] The material thus prepared may include silicon, phosphorus, sulfur, manganese, iron, etc. as inevitable impurities, which may adversely affect the color tone of the decorative surface, and are therefore preferably controlled to within 1% by weight each.

[0078] The titanium nitride powder may be either TiN of stoichiometrical composition, or TiN_{1-x} ($0 < x < 1$) of non-stoichiometrical composition. In order to obtain high wear resistance and a color tone which has high decorative value, purity of each of the powders is preferably 99% or higher. There arises no problem if a part of the titanium nitride powder reacts with the nickel powder thereby forming a small amount of TiNi .

[0079] In order to establish a composition formula of the titanium nitride constituting the ceramics for decorative component as TiN_x ($0.8 \leq x \leq 0.96$), the powder of the titanium nitride of a composition formula TiN_x ($0.7 \leq x \leq 0.9$) may be used.

[0080] Then an organic solvent, for example, isopropyl alcohol, is added to the stock material. The mixture is charged into a mill to be crushed and mixed, with a predetermined amount of paraffin wax added as a binder. The mixture is then formed in a desired shape such as disk, plate, ring, etc. by dry pressure molding process, cold hydrostatic pressure molding process, extrusion molding process or the like. The green compact thus obtained is degreased in a non-oxidizing

atmosphere such as nitrogen or inert gas, as required. The green compact is then fired in an atmosphere of at least one of nitrogen and inert gas or in vacuum, thereby to obtain a sintered material having relative density of 95% or higher.

[0081] In case at least one of molybdenum, niobium, tungsten and tantalum is used, carbon that constitutes the paraffin wax reacts with molybdenum, tungsten and tantalum during firing, so as to form molybdenum carbide, tungsten carbide and tantalum carbide, respectively, which are trapped in nickel.

[0082] The surface of the sintering which is required to have decorative value is lapped on a lapping machine, followed by barrel polishing process. This turns the surface of the sintering into decorative surface having golden color tone comprising the ceramics for decorative component of the present invention.

[0083] The maximum diameter of voids formed on the decorative surface is preferably controlled to 30 μm or less. When the maximum diameter is controlled within the above range, adhesion of various germs, foreign materials and contaminants into the voids can be suppressed.

[0084] In case the product made of the ceramics for decorative component has a complicated shape, the material may be first formed in a block or other convenient shape which resembles the product shape by dry pressure molding process, cold hydrostatic pressure molding process, extrusion molding process, injection molding process or the like, with the resultant green compact being sintered, ground into the product shape and finished by lapping and barrel polishing. Or, alternatively, the material may be formed directly into the product shape by injection molding process, with the resultant green compact being sintered and subjected to lapping and barrel polishing.

[0085] The arithmetic mean height R_a may be controlled to 0.03 μm or less, through lapping process by supplying a diamond paste having small mean particle size onto a lapping stage made of tin. For example, diamond paste having a mean particle size of 1 μm or less may be used. In the polishing process, a rotary barrel polishing machine may be used with a polishing medium made of green carborundum (GC) charged into the rotary barrel polishing machine so as to carry out wet polishing operation for 24 hours.

[0086] The green compact is fired and sintered in an atmosphere of at least one of nitrogen and inert gas or in vacuum because, when fired in oxidizing atmosphere, titanium nitride is oxidized into titanium oxide of which natural white color causes the ceramics for decorative component to have whitish color.

[0087] In case dry pressure molding process is employed, molding pressure is preferably in a range from 49 to 196 MPa since the molding pressure exerts influence on the void ratio of the decorative surface and on Vickers hardness (Hv). When the molding pressure is lower than 49 MPa, the molding pressure is insufficient to consolidate the material powder and obtain a sintering having relative density of 95% or higher, thus resulting in the ceramics for decorative component having a void ratio higher than 3% in the decorative surface and/or Vickers hardness (Hv) lower than 8 GPa.

[0088] When the molding pressure is higher than 196 MPa, service life of the molding die becomes shorter. By setting the molding pressure in a range from 49 MPa to 196 MPa, it is made possible to elongate the service life of the molding die, and control the void ratio of the decorative surface of the ceramics for decorative component within 3% and/or Vickers hardness (Hv) not lower than 8 GPa.

[0089] In case the ceramics for decorative component are obtained by sintering in vacuum, the pressure is preferably 1.33 Pa or lower. When the pressure is higher than 1.33 Pa, titanium nitride is oxidized thus making it impossible to obtain the ceramics for decorative component having golden color tone. When the pressure is set to 1.33 Pa or lower, titanium nitride is not oxidized during firing and therefore the ceramics for decorative component having golden color tone are obtained.

[0090] The sintering temperature is preferably in a range from 1200 to 1800°C. When the sintering temperature is lower than 1200°C, sintering process does not proceed sufficiently and therefore the sintered material having relative density of 95% or higher cannot be obtained, thus resulting in void ratio higher than 3% in the decorative surface of the ceramics for decorative component. When the sintering temperature is higher than 1800°C, crystal grains of the sintered material grow excessively, thus resulting in unfavorable mechanical properties, while the manufacturing cost for sintering increases. The void ratio can be controlled within 3% and the manufacturing cost for sintering can be kept low by controlling the sintering temperature in a range from 1200 to 1800°C.

[0091] The ceramics for decorative component of the present invention thus obtained have high-grade impression and aesthetic satisfaction, and therefore mind soothing effect is obtained through visual sense. Therefore the ceramics for decorative component can be preferably used as the decorative component for watch such as watch case and links of watchband which have highly esteemed beautiful golden color tone, decorative component of accessory such as brooch, necklace, ear ring, ring, necktie pin, tie tack, medal, button, etc., decorative architectural members such as tiles for floor, wall or ceiling, door knob, etc. and decorative component for kitchen utensil such as spoon, fork, etc.

[Examples]

[0092] The present invention will now be described in detail by way of example, but the present invention is not limited to these examples.

[0093] (Example 1)

First, a titanium nitride powder (purity: 99% or higher, mean particle size: 22.3 μm), a nickel powder (purity: 99.5% or higher, mean particle size: 12.8 μm) and powders of vanadium nitride, niobium nitride, tantalum nitride, molybdenum, niobium, tungsten and tantalum (purity: 99.5% or higher, mean particle size: 7 μm) were weighed, crushed and mixed so as to achieve the composition of the sintered material shown in Tables 1 to 3.

[0094] As the comparative example, the main component, the auxiliary component and the additive component that constitute samples Nos. 11, 12, 23, 24, 35, 36, 49 and 50 in Table 1, samples Nos. 63, 64, 77 and 78 in Table 2 and samples Nos. 91, 92 and 94 through 99 shown in Table 3 were weighed and mixed so as to achieve the composition of the sintered material shown in Tables 1 to 3.

[0095] Then isopropyl alcohol was added to the stock material. The mixture was charged into a vibration mill to be crushed and mixed for 72 hours. With 3% by weight of paraffin wax added as a binder, the mixture was dried and turned into a powder by a spray drying method. The powder was subjected to pressure molding under a pressure of 98 MPa to make a green compact which was degreased in a nitrogen atmosphere at 600°C. The green compact was then fired at 1530°C for 2 hours, thereby to obtain disk-shaped sintering measuring 16 mm in diameter.

[0096] Sintered samples Nos. 1 through 99 (excluding samples Nos. 11, 12, 23, 24, 35, 36, 49, 50, 63, 64, 77, 78, 91 and 92) shown in Tables 1 to 3 were lapped on the surface thereof for one hour using diamond abrasive having a mean particle size of 1 μm on a lapping stage made of tin. Then the sintered material was charged into a rotary barrel polishing machine together with water and a polishing medium made of green carborundum (GC) so as to carry out barrel polishing operation for 24 hours, thereby to form the decorative surface. Color tone of the decorative surface was measured according to JIS Z 8722-2000, using a spectrophotometer (CM-3700d, manufactured by Konica Minolta Holdings Inc.) in combination with CIE standard light source of D65 with view angle being set to 10 degrees and the measurement area being set to 3 mm by 5 mm.

[0097] The arithmetic mean height R_a of the decorative surface was measured at 5 points in accordance to JIS B 0601-2001 using a touch probe type surface roughness meter with the measurement length, cut-off point, probe tip radius and scanning speed of the probe being set to 5 mm, 0.8 mm, 2 μm and 0.5 mm/sec, respectively, and the measured values were averaged.

[0098] Sintered samples Nos. 11, 12, 23, 24, 35, 36, 49, 50, 63, 64, 77, 78, 91 and 92 were lapped on the surface thereof using the lapping stage made of tin so as to form the decorative surface. Then, without applying barrel polishing, color tone and arithmetic mean height R_a of the decorative surface was measured by a method similar to that described above.

[0099] The color tone was evaluated by 40 monitors comprising 5 male and 5 female monitors in each of 4 age brackets from 20s to 50s, by responding to questionnaire asking how they felt about 3 qualities of high-grade impression, aesthetic satisfaction and mind soothing effect. Based on these results, the sample was rated as excellent when 90% or more of the monitors responded positively for any of the high-grade impression, aesthetic satisfaction and mind soothing effect, good when the proportion was 80% for at least one item of the qualities, and not good when the proportion was 70% for at least one item of 3 qualities.

[0100] The results are shown in Tables 1 through 3.

Table 1 (Sample marked with * is out of the scope of the present invention.)

Sample No.	Main component		Auxiliary component		Additional component		Mean value of arithmetic mean height Ra (μm)	Lightness index L*	Chromaticness index a*	Chromaticness index b*	High-grade feeling (%)	Aesthetic satisfaction (%)	Mind soothing effect (%)
	Composition	% by weight	Composition	% by weight	Composition	% by weight							
1	TiN	87	Ni	11	VN	2	0.025	72	6	28	80	80	80
2	TiN	91.5	Ni	6	VN	2.5	0.026	75	6	30	90	90	90
3	TiN	88	Ni	6	VN	6	0.025	75	4	31	90	90	90
4	TiN	87	Ni	7	VN	6	0.029	76	9	32	100	100	90
5	TiN	85	Ni	9	VN	6	0.027	76	7	31	100	100	90
6	TiN	83	Ni	11	VN	6	0.028	76	6	31	100	100	90
7	TiN	79.5	Ni	14.5	VN	6	0.024	76	4	32	100	100	90
8	TiN	78	Ni	16	VN	6	0.025	75	4	31	90	100	80
9	TiN	74	Ni	16	VN	10	0.030	79	6	35	90	90	90
10	TiN	78	Ni	11	VN	11	0.028	84	6	36	80	80	80
*11	TiN	85	Ni	9	VN	6	0.040	68	7	18	50	60	70
*12	TiN	83	Ni	11	VN	6	0.043	68	6	18	50	60	70
13	TiN	87	Ni	11	NbN	2	0.024	72	6	28	80	80	80
14	TiN	91.5	Ni	6	NbN	2.5	0.026	75	6	30	90	90	100
15	TiN	88	Ni	6	NbN	6	0.028	75	4	32	90	90	90
16	TiN	87	Ni	7	NbN	6	0.028	76	9	31	100	100	90
17	TiN	85	Ni	9	NbN	6	0.027	76	7	31	100	100	90
18	TiN	83	Ni	11	NbN	6	0.026	76	6	32	100	100	90
19	TiN	79.5	Ni	14.5	NbN	6	0.024	76	4	32	100	100	90
20	TiN	78	Ni	16	NbN	6	0.025	75	4	31	90	100	90
21	TiN	74	Ni	16	NbN	10	0.030	79	6	35	90	90	90
22	TiN	78	Ni	11	NbN	11	0.029	84	6	36	80	80	80
*23	TiN	85	Ni	9	NbN	6	0.038	68	7	18	50	60	70
*24	TiN	83	Ni	11	NbN	6	0.042	67	6	18	50	60	70
25	TiN	87	Ni	11	TaN	2	0.022	72	6	28	80	80	80

Table 1 (continued)

Sample No.	Main component		Auxiliary component		Additional component		Mean value of arithmetic mean height Ra (μm)	Lightness index L*	Chromaticness index a*	Chromaticness index b*	High-grade feeling (%)	Aesthetic satisfaction (%)	Mind soothing effect (%)
	Composition	% by weight	Composition	% by weight	Composition	% by weight							
26	TiN	91.5	Ni	6	TaN	2.5	0.024	75	6	28	90	90	100
27	TiN	88	Ni	6	TaN	6	0.023	75	4	28	90	90	90
28	TiN	87	Ni	7	TaN	6	0.025	76	9	32	100	100	90
29	TiN	85	Ni	9	TaN	6	0.027	76	7	31	100	100	90
30	TiN	83	Ni	11	TaN	6	0.028	76	6	31	100	100	90
31	TiN	79.5	Ni	14.5	TaN	6	0.024	76	4	32	100	100	90
32	TiN	78	Ni	16	TaN	6	0.025	75	4	31	90	100	80
33	TiN	74	Ni	16	TaN	10	0.029	79	6	35	90	90	90
34	TiN	78	Ni	11	TaN	11	0.028	72	6	36	80	80	80
*35	TiN	85	Ni	9	TaN	6	0.038	68	7	18	50	60	70
*36	TiN	83	Ni	11	TaN	6	0.043	67	6	18	50	60	70
37	TiN	87	Ni	11	Mo ₂ C	2	0.025	72	6	28	80	80	80
38	TiN	86.5	Ni	11	Mo ₂ C	2.5	0.026	75	6	28	90	100	100
39	TiN	86	Ni	11	Mo ₂ C	3	0.028	77	6	30	100	100	100
40	TiN	83	Ni	11	Mo ₂ C	6	0.026	78	6	32	100	100	100
41	TiN	81	Ni	11	Mo ₂ C	8	0.025	79	6	34	100	100	100
42	TiN	84	Ni	6	Mo ₂ C	10	0.024	80	4	33	90	100	100
43	TiN	83	Ni	7	Mo ₂ C	10	0.029	81	9	33	90	100	90
44	TiN	81	Ni	9	Mo ₂ C	10	0.028	80	7	34	90	100	90
45	TiN	79	Ni	11	Mo ₂ C	10	0.028	81	6	34	90	100	100
46	TiN	75.5	Ni	14.5	Mo ₂ C	10	0.026	80	4	33	90	90	100
47	TiN	74	Ni	16	Mo ₂ C	10	0.025	81	4	33	90	90	90
48	TiN	78	Ni	11	Mo ₂ C	11	0.030	84	6	36	80	80	80
*49	TiN	85	Ni	9	Mo ₂ C	6	0.040	68	7	18	50	60	70
*50	TiN	83	Ni	11	Mo ₂ C	6	0.045	68	6	18	50	60	70

Table 2 (Sample marked with * is out of the scope of the present invention)

Sample No.	Main component		Auxiliary component		Additional component		Mean value of arithmetic mean height Ra	Lightness index L*	Chromaticness index a*	Chromaticness index b*	High-grade feeling		Aesthetic satisfaction	Mind soothing effect
	Composition	% by weight	Composition	% by weight	Composition	% by weight					(%)	(%)		
51	TiN	87	Ni	11	NbC	2	0.025	72	6	28	80	80	80	80
52	TiN	86.5	Ni	11	NbC	2.5	0.026	75	6	28	90	100	100	100
53	TiN	86	Ni	11	NbC	3	0.026	77	6	30	100	100	100	100
54	TiN	83	Ni	11	NbC	6	0.025	78	6	32	100	100	100	100
55	TiN	81	Ni	11	NbC	8	0.030	79	6	34	100	100	100	100
56	TiN	84	Ni	6	NbC	10	0.026	82	4	33	90	100	100	100
57	TiN	83	Ni	7	NbC	10	0.029	81	9	33	90	100	100	90
58	TiN	81	Ni	9	NbC	10	0.027	82	7	34	90	100	100	90
59	TiN	79	Ni	11	NbC	10	0.028	81	6	34	90	100	100	100
60	TiN	75.5	Ni	14.5	NbC	10	0.026	82	5	33	90	90	100	100
61	TiN	74	Ni	16	NbC	10	0.025	82	4	33	90	90	90	90
62	TiN	78	Ni	11	NbC	11	0.028	84	6	36	80	80	80	80
*63	TiN	85	Ni	9	NbC	6	0.039	68	7	18	50	60	70	70
*64	TiN	83	Ni	11	NbC	6	0.045	67	6	18	50	60	70	70
65	TiN	87	Ni	11	WC	2	0.025	72	6	28	80	80	80	80
66	TiN	86.5	Ni	11	WC	2.5	0.026	75	6	28	90	100	100	100
67	TiN	86	Ni	11	WC	3	0.027	77	6	30	100	100	100	100
68	TiN	83	Ni	11	WC	6	0.028	78	6	32	100	100	100	100
69	TiN	81	Ni	11	WC	8	0.026	79	6	34	100	100	100	100
70	TiN	84	Ni	6	WC	10	0.023	82	4	33	90	100	100	100
71	TiN	83	Ni	7	WC	10	0.029	81	9	33	90	100	90	90
72	TiN	81	Ni	9	WC	10	0.024	82	7	34	90	100	100	90
73	TiN	79	Ni	11	WC	10	0.027	81	6	34	90	100	100	100
74	TiN	75.5	Ni	14.5	WC	10	0.024	82	4	33	90	90	100	100
75	TiN	74	Ni	16	WC	10	0.028	82	4	33	90	90	90	90
76	TiN	78	Ni	11	WC	11	0.028	84	6	36	80	80	80	80
*77	TiN	85	Ni	9	WC	6	0.040	68	7	18	50	60	70	70
*78	TiN	83	Ni	11	WC	6	0.044	68	6	18	50	60	60	70

Table 3 (Sample marked with * is out of the scope of the present invention.)

Sample No.	Main component		Auxiliary component		Additional component		Mean value of arithmetic mean height Ra	Lightness index L*	Chromaticness index a*	Chromaticness index b*	High-grade feeling (%)	Aesthetic satisfaction (%)	Mind soothing effect (%)
	Composition	% by weight	Composition	% by weight	Composition	% by weight							
79	TiN	87	Ni	11	TaC	2	0.023	81	6	28	80	80	80
80	TiN	86.5	Ni	11	TaC	2.5	0.027	75	6	28	90	100	100
81	TiN	86	Ni	11	TaC	3	0.025	77	6	30	100	100	100
82	TiN	83	Ni	11	TaC	6	0.026	78	6	32	100	100	100
83	TiN	81	Ni	11	TaC	8	0.027	79	6	34	100	100	100
84	TiN	84	Ni	6	TaC	10	0.024	82	4	33	90	100	100
85	TiN	83	Ni	7	TaC	10	0.028	81	9	33	90	100	90
86	TiN	81	Ni	9	TaC	10	0.027	82	7	34	90	100	90
87	TiN	79	Ni	11	TaC	10	0.028	81	6	34	90	100	100
88	TiN	75.5	Ni	14.5	TaC	10	0.029	82	4	33	90	90	100
89	TiN	74	Ni	16	TaC	10	0.025	82	4	33	90	90	90
90	TiN	78	Ni	11	TaC	11	0.030	84	6	36	80	80	80
*91	TiN	85	Ni	9	TaC	6	0.040	68	7	18	50	60	70
*92	TiN	83	Ni	11	TaC	6	0.041	67	6	18	50	60	70
93	TiN	83	Ni	11	VN	3	0.025	79	7	34	100	100	100
*94	ZrO ₂	80	Ni	10	Mo ₂ C	3	0.03	67	1	39	60	50	60
					Y ₂ O ₃	10							
					TiC	30							
*95	TiN	42.5	Ni	16.5	Cr ₃ C ₂	8	0.027	68	3	6	30	30	30
					Mo ₂ C	3							
					TiC	25.5							
*96	TiN	47.5	Ni	14	Cr ₃ C ₂	12	0.027	68	10	7	30	30	30
*97	CeO ₂	100	-	-	Mo ₂ C	1	0.027	96	-1	10	50	50	50
					Pr ₆ O ₁₁	0.0005							
					AlN	10							
*98	TiN	80	Ni	10	Si	10	0.030	64	5	16	50	50	50
*99	TiN	80	Ni	10			0.030	64	5	15	50	50	50

[0101] As will be seen from the results shown in Tables 1 through 3, sample No. 98 which contained aluminum nitride as the additive component and sample No. 99 which contained silicon could not satisfy the monitors and were evaluated as not good, as the value of lightness index L^* was less than 72 and the value of chromaticness index b^* was less than 28.

[0102] Sample No. 94 which contained zirconium oxide as the main component could not satisfy the monitors and were evaluated as not good, as the value of chromaticness index b^* exceeded 36.

[0103] Sample No. 97 which contained cerium oxide as the main component could not satisfy the monitors and were evaluated as not good, as the value of lightness index L^* exceeded 84.

[0104] Samples Nos. 95 and 96 which contained 25.5 to 30% by weight of titanium carbide as the additional component could not satisfy the monitors and were evaluated as not good, as the value of lightness index L^* was less than 72 and chromaticness index b^* was less than 28.

[0105] Samples Nos. 11, 12, 23, 24, 35, 36, 49, 50, 63, 64, 77, 78, 91 and 92 of which decorative surfaces had arithmetic mean height R_a larger than $0.03\text{ }\mu\text{m}$ could not satisfy the monitors and were evaluated as not good, as the value of lightness index L^* was less than 72 and chromaticness index b^* was less than 28.

[0106] Samples Nos. 1 through 10, 13 through 22, 25 through 34, 37 through 48, 51 through 62, 65 through 76, 79 through 90 and 93 of which decorative surfaces had arithmetic mean height R_a not larger than $0.03\text{ }\mu\text{m}$, lightness index L^* in a range from 72 to 84 and the values of chromaticness indices a^* and b^* in ranges from 4 to 9 and from 28 to 36, respectively, satisfied the monitors with high-grade impression, aesthetic satisfaction and mind soothing effect, and were rated as excellent or good.

[0107] Comparison of samples No. 5 and No. 11 or No. 6 and No. 12 of the same compositions shows that samples No. 5 and No. 6, both having arithmetic mean height R_a of the decorative surface not larger than $0.03\text{ }\mu\text{m}$, were rated higher with higher value of chromaticness index b^* than samples No. 11 and No. 12.

[0108] Samples Nos. 4 through 7, 16 through 19, 28 through 31, 38 through 41, 43 through 46, 52 through 55, 57 through 60, 66 through 69, 71 through 74, 80 through 83, 85 through 88 and 93 which contained 7 to 14.5% by weight of nickel and 2.5 to 10% by weight of at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide, in particular, were rated even better, as excellent.

[0109] Samples Nos. 53 through 55, 67 through 69, 81 through 83 and 93 which contained 3 to 8% by weight of at least one of niobium carbide, molybdenum carbide, tungsten carbide and tantalum carbide were rated as perfect, with 100% of the monitors responded positively for every item of quality.

[0110] (Example 2)

First, a titanium nitride powder (purity: 99% or higher, mean particle size: $22.3\text{ }\mu\text{m}$), a nickel powder (purity: 99.5% or higher, mean particle size: $12.8\text{ }\mu\text{m}$), a niobium carbide powder (purity: 99.5% or higher, mean particle size: $7\text{ }\mu\text{m}$) and a chromium powder (purity: 99% or higher, mean particle size: $40\text{ }\mu\text{m}$) were weighed, crushed and mixed so as to achieve the composition of the sintered material shown in Table 4.

[0111] Then isopropyl alcohol solution was added to the stock material. The mixture was charged into a vibration mill to be crushed and mixed for 72 hours. With 3% by weight of paraffin wax added as a binder, the mixture was dried and turned into a powder by a spray drying method. The powder was subjected to pressure molding under a pressure of 98 MPa to make a green compact which was degreased in a nitrogen atmosphere at 600°C . The green compact was then fired at 1530°C for 2 hours, thereby to obtain disk-shaped sintering measuring 16 mm in diameter.

[0112] Sintered samples Nos. 100 through 104 shown in Table 4 were lapped on the surface thereof for one hour using diamond abrasive having a mean particle size of $1\text{ }\mu\text{m}$ on a lapping stage made of tin. Then the sintered material was charged into a rotary barrel polishing machine together with water and a polishing medium made of green carborundum (GC) so as to carry out barrel polishing operation for 24 hours, thereby to form the decorative surface. Color tone of the decorative surface was measured according to JIS Z 8722-2000, using a spectrophotometer (CM-3700d, manufactured by Konica Minolta Holdings Inc., etc.) in combination with CIE standard light source of D65 with the view angle being set to 10 degrees and the measurement area set to 3 mm by 5 mm .

[0113] The number of atoms x in TiN_x was determined by measuring the proportions of oxygen, nitrogen and carbon to titanium nitride in terms of percentage by weight by means of an oxygen-nitrogen analyzer and a carbon analyzer. Then the total content of these elements was subtracted from the amount of titanium nitride in 100% by weight, and the remainder was divided by the atomic weight 47.9 of titanium, thereby to obtain the number of titanium atoms included in TiN_x . The number of nitrogen atoms in TiN_x was determined by dividing the proportion of nitrogen by the atomic weight 14 of nitrogen. Number of nitrogen atoms when the number of titanium atoms was assumed to be 1 was taken as the number of atoms x .

[0114] The arithmetic mean height R_a of the decorative surface was measured at 5 points in accordance to JIS B 0601-2001 using a touch probe type surface roughness meter with the measurement length, cut-off point, probe tip radius and scanning speed of the probe being set to 5 mm , 0.8 mm , $2\text{ }\mu\text{m}$ and 0.5 mm/sec , respectively, and the measured values were averaged.

[0115] The color tone was evaluated by 40 monitors comprising 5 male and 5 female monitors in each of 4 age brackets from 20s to 50s, by responding to questionnaire asking how they felt about 3 items of quality of high-grade impression,

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aesthetic satisfaction and mind soothing effect. The proportion of monitors who responded positively for each item of quality is shown in Table 4. The results are shown in Table 4.

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Table 4

Sample No.	Main component		Auxiliary component		Additional component		Additional component	
	Composition	x	% by weight	Composition	% by weight	Composition	% by weight	% by weight
105	TiNx	0.7	78.5	Ni	14	NbC	6	Cr
106		0.8						
107		0.9						
108		0.96						
109		0.99						
								1.5

Table 4 (continued)

Sample No.	Mean value of arithmetic mean height Ra (μm)	Lightness index L*	Chromaticness index a*	Chromaticness index b*	High-grade feeling (%)	Aesthetic satisfaction (%)	Mind soothing effect (%)
105	0.028	78	4	28	100	80	80
106	0.025	77	4	28	100	100	90
107	0.027	76	4	28	100	100	90
108	0.025	75	4	30	100	100	90
109	0.029	73	4	32	80	80	90

As will be seen from the results shown in Table 4, samples No. 101 through 103 of which number of atoms is not less than 0.8 and not more than 0.96 could attain high evaluation due to monitors in high-grade impression and aesthetic satisfaction, as compared with samples 100 and 104 of which number of atoms is not within the above range.

[0116] (Example 3)

First, a titanium nitride powder (purity: 99% or higher, mean particle size: 22.3 μm), a nickel powder (purity: 99.5% or higher, mean particle size: 12.8 μm), a molybdenum powder (purity: 99.5% or higher, mean particle size: 7 μm) and a chromium powder (purity: 99% or higher, mean particle size: 40 μm) were weighed, crushed and mixed so as to achieve the composition of the sintered material shown in Table 5. Duration of crushing and mixing operation is shown in Table 5.

[0117] Then isopropyl alcohol solution was added to the stock material. The mixture was charged into a vibration mill to be crushed and mixed for 72 hours. With 3% by weight of paraffin wax added as a binder, the mixture was dried and turned into a powder by a spray drying method. The powder was subjected to pressure molding under a pressure of 98 MPa to make a green compact which was degreased in a nitrogen atmosphere at 600°C. The green compact was then fired at 1530°C for 2 hours, thereby to obtain disk-shaped sintering measuring 16 mm in diameter.

[0118] Sintered samples Nos. 105 through 109 shown in Table 5 were lapped on the surface thereof for one hour using diamond abrasive having a mean particle size of 1 μm on a lapping stage made of tin. Then the sintered material was charged into a rotary barrel polishing machine together with water and a polishing medium made of green carborundum (GC) so as to carry out barrel polishing operation for 24 hours, thereby to form the decorative surface. Color tone of the decorative surface was measured according to JIS Z 8722-2000, using a spectrophotometer (CM-3700d, manufactured by Konica Minolta Holdings Inc., etc.) in combination with CIE standard light source of D65 with the view angle being set to 10 degrees and the measurement area set to 3 mm by 5 mm

[0119] The arithmetic mean height R_a of the decorative surface was measured at 5 points in accordance to JIS B 0601-2001 using a touch probe type surface roughness meter with the measurement length, cut-off point, probe tip radius and scanning speed of the probe being set to 5 mm, 0.8 mm, 2 μm and 0.5 mm/sec, respectively, and the measured values were averaged.

[0120] Then samples Nos. 100 through 104 were subjected to partial immersion in artificial sweat test (leaving for 24 hours at $23 \pm 2^\circ\text{C}$), among the corrosion resistance test methods specified in JIS B 7001-1995, and the color tone of the decorative surface was measured by the method described previously before and after the test.

[0121] Results of the measurements are shown Tables 5 and 6.

Table 5

Sample No.	Main component		Auxiliary component		Additional component		Additional component	
	Composition	% by weight	Composition	% by weight	Composition	% by weight	Composition	% by weight
105	TiN	85	Ni	10	Mo ₂ C	5	Cr	0
106	TiN	83.5	Ni	10	Mo ₂ C	5	Cr	1.5
107	TiN	81	Ni	10	Mo ₂ C	5	Cr	4
108	TiN	78.5	Ni	10	Mo ₂ C	5	Cr	6.5
109	TiN	77.5	Ni	10	Mo ₂ C	5	Cr	7.5

Table 6

Mean value of arithmetic mean height R_a (μm)	Lightness index L^*			Chromaticness index a^*			Chromaticness index b^*		
	Before test	After test	Difference	Before test	After test	Difference	Before test	After test	Difference
0.028	78.0	75.7	2.3	6.0	6.6	-0.6	31.0	30.9	0.1
0.026	77.8	77.7	0.1	5.8	5.7	0.1	29.8	29.7	0.1
0.028	77.5	77.5	0.0	5.5	5.4	0.1	29.4	29.4	0.0
0.027	77.4	77.4	0.0	5.2	5.1	0.1	29.0	28.9	0.1

(continued)

Mean value of arithmetic mean height Ra (μm)	Lightness index L*			Chromaticness index a*			Chromaticness index b*		
	Before test	After test	Difference	Before test	After test	Difference	Before test	After test	Difference
0.027	77.0	77.0	0.0	4.0	4.0	0.0	28.0	28.0	0.0

[0122] As can be seen from the results shown Tables 5 and 6, samples Nos. 106 through 109 which contained chromium showed less variation in the lightness index L* and chromaticness indices a*, b* after the test than sample No. 105 which did not contain chromium showed, and demonstrated better corrosion resistance and capability to maintain high-grade impression, aesthetic satisfaction and mind soothing effect over a long period of time.

[0123] Sample 109 which included much chromium content had good corrosion resistance but showed lower values of chromaticness indices a* and b* that indicate clearness. Thus samples Nos. 106 through 108 which included chromium content of 1.5% by weight or more and not more than 6.5% by weight are better in providing both corrosion resistance and clear color tone.

[0124] (Example 4)

First, a titanium nitride powder (purity 99% or higher, mean particle size: 22.3 μm), a nickel powder (purity: 99.5% or higher, mean particle size: 12.8 μm), molybdenum and tantalum powders (purity: 99.5% or higher, mean particle size: 7 μm) were weighed, crushed and mixed so as to achieve the composition of the sintered material shown in Table 7.

[0125] Then isopropyl alcohol solution was added to the stock material. The mixture was charged into a vibration mill to be crushed and mixed for 72 hours. With 3% by weight of paraffin wax added as a binder, the mixture was dried and turned into a powder by a spray drying method. The powder was subjected to pressure molding under a pressure of 98 MPa to make a green compact which was degreased in a nitrogen atmosphere at 600°C. The green compact was then fired at 1600°C for 2 hours, thereby to obtain disk-shaped sintering measuring 16 mm in diameter.

[0126] The sintered materials were lapped on the surface thereof on a lapping stage made of tin. Then the sintered material was charged into a rotary barrel polishing machine together with water and polishing medium made of green carborundum (GC) so as to carry out barrel polishing operation while adjusting the duration, thereby controlling the void ratio of the decorative surface to obtain samples Nos. 110 through 117 shown in Table 7. Color tone of the decorative surface and arithmetic mean height Ra of the decorative surface were measured similarly to Example 1.

Void ratio in the decorative surface was determined by capturing an image of the decorative surface with a CCD camera under a metallurgical microscope with a magnifying power of 200 times, and measuring at 20 points in one field of view, with measuring area of one field of view in the image being set to $2.25 \times 10^{-2} \text{ mm}^2$, number of fields of view set to 20 and total measuring area to $4.5 \times 10^{-1} \text{ mm}^2$, by using an image analyzer (LUZEX-FS, manufactured by NIRECO Corporation). That is, measuring of one field of view was made at 20 positions, and the void ratio was determined for the sum of the measurement areas.

[0127] The color tone was evaluated by 40 monitors comprising 5 male and 5 female monitors in each of 4 age brackets from 20s to 50s, by responding to questionnaire asking how they felt about 3 qualities of high-grade impression, aesthetic satisfaction and mind soothing effect. Proportion of monitors who responded positively or each item of quality is shown in Table 7.

Table 7

Sample No.	Mean value of arithmetic mean height Ra (μm)	Void ratio (%)	Main component		Auxiliary component		Additional component		Lightness index L*	Chromaticness index a*	Chromaticness index b*	High-grade feeling (%)	Aesthetic satisfaction (%)	Mind soothing effect (%)
			Composition	% by weight	Composition	% by weight	Composition	% by weight						
110	0.030	4.0	TiN	82	Ni	11	Mo ₂ C	7	72	6	33	90	100	90
111	0.025	3.0	TiN	82	Ni	11	Mo ₂ C	7	75	6	34	100	100	90
112	0.018	2.0	TiN	82	Ni	11	Mo ₂ C	7	77	6	35	100	100	90
113	0.011	1.0	TiN	82	Ni	11	Mo ₂ C	7	79	6	36	100	100	90
114	0.030	4.0	TiN	82	Ni	11	TaC	7	72	6	33	90	100	90
115	0.025	3.0	TiN	82	Ni	11	TaC	7	75	6	34	100	100	90
116	0.018	2.0	TiN	82	Ni	11	TaC	7	77	6	35	100	100	90
117	0.011	1.0	TiN	82	Ni	11	TaC	7	79	6	36	100	100	90

[0128] As can be seen from the results shown in Table 7, samples Nos. 111 through 113 and 115 through 117 having a void ratios not higher than 3% showed lightness index L^* in a range from 75 to 79, higher than those of samples Nos. 110 and 114. As a result, the monitors felt high-grade impression more from samples Nos. 111 through 113 and 115 through 117 than from samples Nos. 110 and 114.

[0129] It can also be seen that the value of chromaticness index b^* becomes higher as the arithmetic mean height R_a decreases. Thus it was verified that satisfactory golden color can be realized by controlling the arithmetic mean height R_a within $0.03\ \mu\text{m}$.

Claims

1. Ceramics for decorative component comprising titanium nitride as a main component, nickel as an auxiliary component, and at least one selected from a group consisting of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as an additional component, wherein at least arithmetic mean height R_a of the decorative surface is $0.03\ \mu\text{m}$ or less, and the decorative surface has such a color tone that lightness index L^* is in a range from 72 to 84, and chromaticness indices a^* and b^* are from 4 to 9 and 28 to 36, respectively, in the $L^*a^*b^*$ color space of CIE1976.
2. The ceramics for decorative component according to claim 1, wherein the titanium nitride has a composition formula of TiN_x ($0.8 \leq x \leq 0.96$).
3. The ceramics for decorative component according to claim 1 or 2, further containing chromium as the additional component.
4. The ceramics for decorative component according to any one of claims 1 to 3, which contain 7% or more and not more than 14.5% by weight of nickel as the auxiliary component and 2.5% or more and not more than 10% by weight of at least one of vanadium nitride, niobium nitride, tantalum nitride, molybdenum carbide, niobium carbide, tungsten carbide and tantalum carbide as the additional component.
5. The ceramics for decorative component according to any one of claims 1 to 4, which contains 1.5% or more and not more than 6.5% by weight of chromium as the additional component.
6. The ceramics for decorative component according to any one of claims 1 to 5, wherein the additional component is at least one of niobium carbide, molybdenum carbide, tungsten carbide and tantalum carbide, of which content is 3% or more and not more than 8% by weight.
7. The ceramics for decorative component according to any one of claims 1 to 6, wherein a void ratio in the decorative surface is 3% or less.
8. A decorative component for a watch, which is made of the ceramics for decorative component according to any one of the claims 1 to 7.

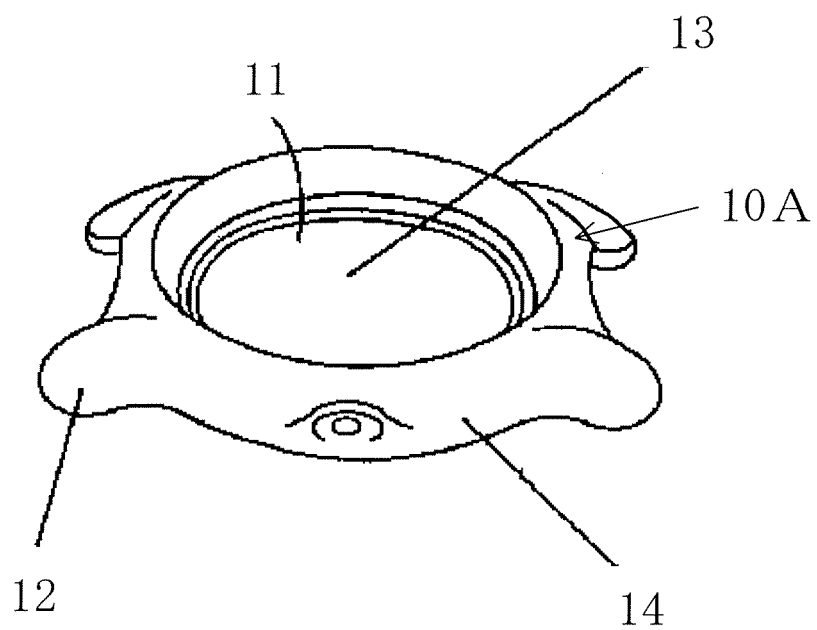


Fig. 1 (a)

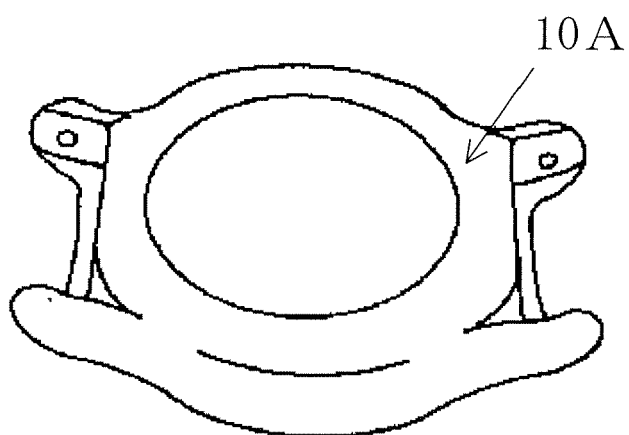


Fig. 1 (b)

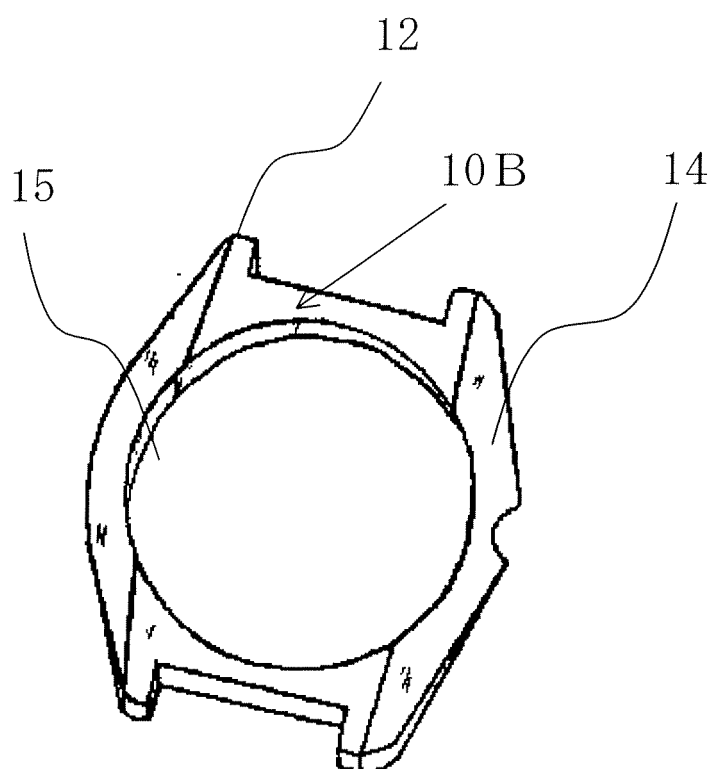


Fig. 2

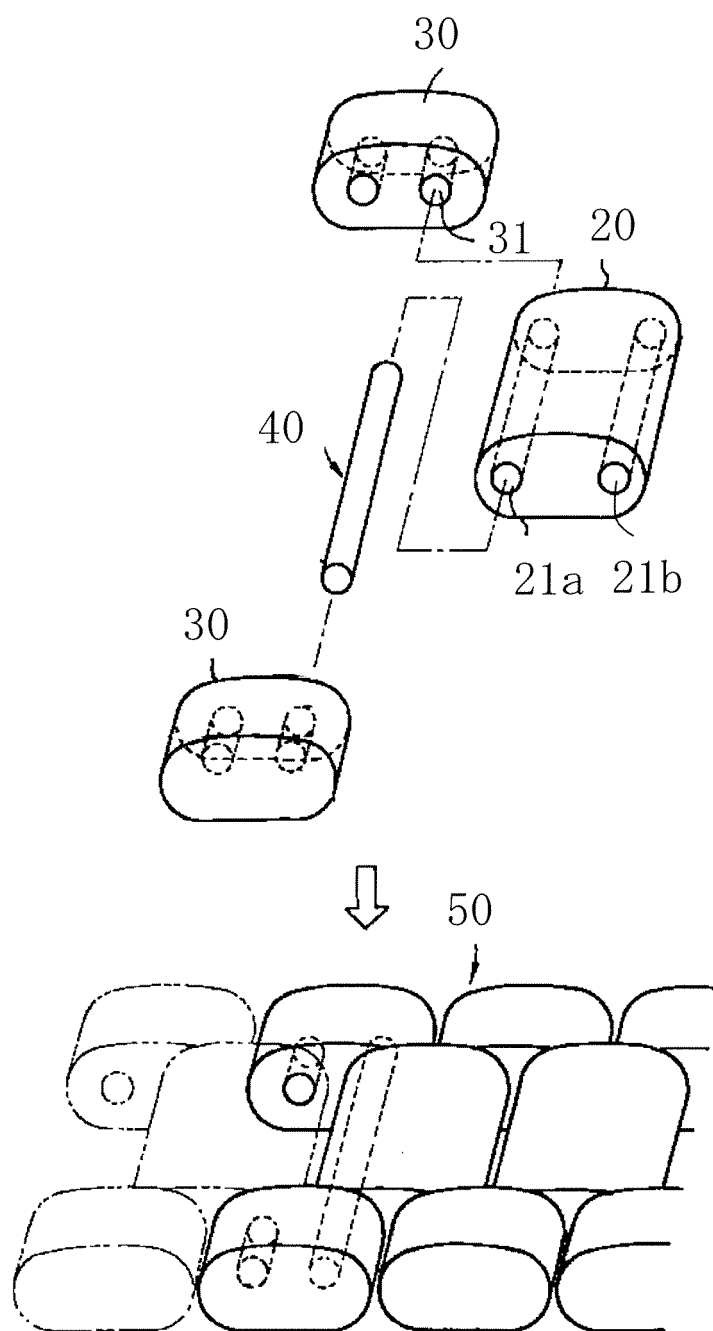


Fig. 3



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