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(54) **CERMET ORNAMENT MEMBER, AND WATCH, PORTABLE TERMINAL, AND ACCESSORY OBTAINED USING SAME**

ZIERELEMENT AUS CERMET UND UHR, TRAGBARES ENDGERÄT UND DARAUS ERHALTENES ZUBEHÖR

ÉLÉMENT DÉCORATIF EN CERMET, ET MONTRE, TERMINAL PORTATIF, ET ACCESSOIRE OBTENUS AU MOYEN DE CELUI-CI

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## Description

**[0001]** The present invention relates to a cermet decorative member, and a watch, a mobile terminal, and an accessory obtained using the same.

### Background Art

**[0002]** Conventionally, gold, gold alloys, or various plated metals have been used in decorative parts exhibiting a gold color from the perspectives of color tone and corrosion resistance. However, because gold, gold alloys, and plated metal materials all have low hardness, there is a problem that contact with hard substances causes damage or deformation of the surface.

**[0003]** To solve this problem and to respond to diversification of consumer preferences, the present inventors have proposed various cermet decorative members exhibiting a gold color.

**[0004]** For example, WO 2009/069549 (Patent Document 1) proposes a cermet decorative member which is a ceramic for a decorative part including a titanium nitride sintered compact including titanium nitride as a primary component, wherein the member contains nickel, niobium, chromium, and carbon, and the carbon content is not less than 0.5 mass% and not greater than 0.9 mass%.

**[0005]** Furthermore, WO 2009/145146 (Patent Document 2) proposes a cermet decorative member, which includes a ceramic for a decorative part including a titanium nitride sintered compact, wherein the ceramic contains nickel, niobium, chromium, and carbon, and the carbon content is not less than 1 mass% and not greater than 2 mass%.

**[0006]** Furthermore, EP 2298948 A1 (Patent Document 3) proposes ceramics for a decorative component composed of a titanium nitride-based sintered body, wherein the titanium nitride-based sintered body contains nickel, niobium, chromium, and carbon having a content of not less than 1% by mass nor more than 2% by mass.

**[0007]** Furthermore, EP 2568055 A1 (Patent Document 4) proposes a lightweight material for decorative parts having a silver metallic color tone including a sintered body having a main hard phase composed of a solid solution formed of titanium carbonitride and titanium carbide, a main binder phase composed of nickel, a first additive material composed of at least one selected from the group consisting of molybdenum carbide, niobium carbide, tungsten carbide, and tantalum carbide, a second additive material composed of at least one of chromium and chromium carbide, and the balance being incidental impurities.

**[0008]** Furthermore, JP 2011130894 A (Patent Document 5) proposes a molded piece for an ornamental part comprising a titanium nitride material including nickel, niobium, chromium, and carbon.

### Summary of Invention

**[0009]** The present invention is directed at a cermet decorative member according to independent claim 1. Furthermore, the present invention is directed at a watch, a mobile terminal, and an accessory according to independent claims 2 to 4.

**[0010]** Preferred embodiments are described in the dependent claims.

### Brief Description of Drawings

**[0011]**

FIGS. 1A and 1B illustrate a watch case as an example of a cermet decorative member of the present embodiment. FIG. 1A is a perspective view seen from the front side, and FIG. 1B is a perspective view seen from the rear side.

FIG. 2 is a schematic view illustrating an example of a configuration of a watchband as an example of a cermet decorative member of the present embodiment.

### Description of Embodiments

**[0012]** In recent years, a demand in reduction in color variation of a cermet decorative member is increasing in order to provide a consumer with the greater luxury feel and a more esthetically pleasing look.

**[0013]** Description will be given below of an example of a cermet decorative member of the present embodiment.

**[0014]** The cermet decorative member includes a cermet containing a crystal phase including titanium carbonitride and a bonding phase including metal. The bonding phase contains nickel as the primary component and at least niobium and chromium, wherein the lattice constant of the nickel is not less than 3.54 Å. Here, the primary component in the bonding phase is a component exceeding 50 mass% per 100 mass% of components constituting the bonding phase.

**[0015]** The cermet decorative member of the present embodiment satisfying the configuration above exhibits a color tone in the gold family with little color variation. Here, the lattice constant of nickel single crystal is 3.5238 Å, whereas the lattice constant of nickel in the cermet decorative member of the present embodiment is not less than 3.54 Å. It is surmised that the cermet decorative member of the present embodiment exhibits a color tone in the gold family with little color variation because at least one of niobium and chromium forms a solid solution with nickel, which is the primary component of the bonding phase and has a high ionization tendency, and this reduces the ionization tendency of nickel. In particular, it is surmised that niobium forming a solid solution has a large effect.

**[0016]** It is known that the lattice constant of nickel in the cermet decorative member of the present embodiment can be measured using an X-ray diffractometer (XRD; e.g., D8 ADVANCE, manufactured by Bruker AXS GmbH).

**[0017]** In the cermet decorative member of the present embodiment, nickel is from 7.0 to 11.0 mass%, niobium is from 1.5 to 6.0 mass%, chromium is from 1.0 to 5.0 mass%, and the remainder is titanium carbonitride per 100 mass% of all components that constitute the cermet. More preferably, nickel is from 8.0 to 10.0 mass%, niobium is from 2.5 to 5.0 mass%, and chromium is from 2.0 to 4.0 mass%. Note that the presence or absence of titanium carbonitride in the cermet decorative member of the present embodiment may be verified by XRD measurement and identification. Furthermore, the presence of nickel, niobium, and chromium in a portion other than the crystal phase can be verified by observation by a scanning electron microscope (SEM), and by using an EDS equipped with the SEM.

**[0018]** The contents of nickel, niobium, and chromium may be determined by measurement using an inductively coupled plasma emission spectrophotometer (ICP) or a fluorescent X-ray analyzer (XRF). The titanium carbonitride content may be determined by subtracting the sum of nickel, niobium, and chromium contents from 100 mass%. The titanium carbonitride content may also be determined by measuring Ti by ICP or XRF, and adding up the results of measuring carbon using a carbon analyzer and nitrogen measured using a nitrogen analyzer.

**[0019]** From the nickel content and the sum of nickel, niobium, and chromium contents, it can be verified whether or not nickel is the primary component.

**[0020]** Next, color variation may be confirmed by the following method. First, in measurement, the sample is lapped to form a lapped face of which the arithmetic mean roughness Ra on the roughness curve is not greater than 0.03 $\mu$m. Then, using a spectrophotometric colorimeter (CM-5, manufactured by Konica Minolta Inc.), the lightness of the color L* (also simply called "L*" hereinafter), psychometric chroma coordinate a* (also simply called "a*" hereinafter) and psychometric chroma coordinate b* (also simply called "b*" hereinafter) in the CIE 1976 L*a*b* color space are determined according to JIS Z 8722-2000. As measurement conditions, SCI (specular component included) conditions may be used, a CIE standard light source D65 may be used as a light source, the illumination receiving mode may be di: 8°·de: 8° (diffuse illumination·8° direction reception), and the measurement diameter may be 3 mm.

**[0021]** Then, measurement may be performed in at least three locations on a single cermet decorative member, and color variation may be determined by the formula $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ using the obtained values of L*, a*, and b*.

**[0022]** Here, L* is an index of brightness expressing the lightness and darkness of a color tone. The larger value of L* indicates a bright color tone, while the smaller value of L* indicates the darker color tone.

**[0023]** Furthermore, a* is an index expressing the position between red and green of a color tone. If a* is a large positive value, the color tone is in the red family, and if it is a large negative value, the color tone is in the green family.

**[0024]** Additionally, b* is an index expressing the position between yellow and blue of a color tone. If b* is a large positive value, the color tone is in the yellow family, and if it is a large negative value, the color tone is in the blue family.

**[0025]** Because the absolute values of a* and b* are also indices expressing the intensity of color tone, when the absolute values of a* and b* are low, it is a subdued color tone of suppressed intensity.

**[0026]** In the cermet decorative member of the present embodiment, when the lattice constant of the titanium carbonitride crystal phase has a lattice constant of 4.27 Å or more and 4.30 Å or less, the above L* is not less than 64 and not greater than 68, a* is not less than 1 and not greater than 4, and b* is not less than 1 and not greater than 5. As such, a member exhibiting a purple-tinged gold color tone may be obtained.

**[0027]** Furthermore, in the cermet decorative member of the present embodiment, when the cermet contains at least one of molybdenum, tungsten, and cobalt, they act as sintering aids and the firing temperature can be reduced. As a result, a decrease in shape workability due to abnormal grain growth of titanium carbonitride can be suppressed.

**[0028]** Additionally, the cermet contains at least one of molybdenum, tungsten, and cobalt. The contents are not less than 0.5 mass% and not greater than 2.0 mass% of molybdenum, not less than 0.05 mass% and not greater than 0.4 mass% of tungsten, and not less than 0.02 mass% and not greater than 0.2 mass% of cobalt, per 100 mass% of all components constituting the cermet. Preferably, the sum of molybdenum, tungsten, and cobalt contents is not greater than 2 mass%. The cermet contains all of molybdenum, tungsten, and cobalt.

**[0029]** The contents of molybdenum, tungsten, and cobalt per 100 mass% of all components constituting the cermet may be measured using ICP or XRF.

**[0030]** Additionally, in the cermet decorative member of the present embodiment, when the oxygen content is less than 1.0 mass% per 100 mass% of all components constituting the cermet, there is little oxidation of the bonding phase, and color variation can therefore be further reduced. Furthermore, when the oxygen content is less than 1.0 mass%, there is little oxidation of the bonding phase, i.e. nickel, niobium, chromium, and the like are present as metals. As a result, it can play a sufficient role as a bonding phase. The oxygen content may be determined by measurement using an oxygen analyzer (e.g., TCH-600, manufactured by LECO Corporation).

**[0031]** Furthermore, in the cermet decorative member of the present embodiment, when the free carbon content is not less than 1.5 mass% and not greater than 2.5 mass% per 100 mass% of all components constituting in the cermet, the shape processing time for making the desired shape can be reduced while mechanical characteristics as a decorative member are maintained. Free carbon content may be determined by measurement using a carbon analyzer (e.g., RC-612, manufactured by LECO Corporation).

**[0032]** A Compound including nickel and chromium may also be present in the cermet decorative member of the present embodiment. Nickel and chromium are magnetic, whereas a compound including nickel and chromium is non-magnetic. Thus, when the compound including nickel and chromium is present, it tends not to have a magnetic effect when the cermet decorative member is used in a watch, mobile terminal, or the like.

**[0033]** Here, the presence of the compound including nickel and chromium may be verified by measurement and identification by XRD. A compound including nickel and chromium indicates a compound represented as CrNi. The JCPDS number of CrNi is 01-071-7594.

**[0034]** The cermet decorative member of the present embodiment has three-point bending strength of not less than 1000 MPa, and has sufficient mechanical characteristics for practical use. Three-point bending strength may be measured according to JIS R 1601-2008.

**[0035]** Next, a specific example of the cermet decorative member of the present embodiment will be described.

**[0036]** FIGS. 1A and 1B illustrate a watch case as an example of a cermet decorative member of the present embodiment. FIG. 1A is a perspective view seen from the front side, and FIG. 1B is a perspective view seen from the rear side. FIG. 2 is a schematic view illustrating an example of a configuration of a watchband as an example of a cermet decorative member of the present embodiment.

**[0037]** The watch case 10 illustrated in FIGS. 1A and 1B includes a recessed portion 11 housing a movement (drive mechanism) and the like (not illustrated), and lug portions 12 which affix a watchband (not illustrated) for wearing the watch on the wrist. The recessed portion 11 is made from a thin bottom portion 13 and a thick torso portion 14.

**[0038]** The band pieces constituting the watchband 50 illustrated in FIG. 2 are configured from center pieces 20 each having through-holes 21 into which pins 40 are inserted, and outer pieces 30 arranged so as to sandwich the center pieces 20, each of the outer pieces 30 having pin holes 31 through which the pins 40 are inserted. The watchband 50 is configured by the center pieces 20 and the outer pieces 30 being sequentially connected by means of the pins 40 being inserted in the through-holes 21 of the center pieces 20 and both ends of the inserted pins 40 being inserted into the pin holes 31 of the outer pieces 30.

**[0039]** The watch case 10 and the band pieces constituting the watchband 50 including the cermet decorative member of the present embodiment can exhibit a color tone in the gold family with little color variation, and as a result, provide a consumer with a luxury feel and an esthetically pleasing look. Needless to say, a watch including the cermet decorative member of the present embodiment in the watch case 10, the band pieces constituting the watchband 50, and the like can also provide a consumer with a luxury feel and an esthetically pleasing look. Furthermore, the cermet decorative member of the present embodiment may also be used in the hands and face of a watch.

**[0040]** The cermet decorative member of the present embodiment may also be suitably used in cases, various operation keys, and the like of mobile terminals. As such, it provides a consumer who owns the mobile terminal including the cermet decorative member of the present embodiment with a luxury feel and esthetically pleasing look. A mobile terminal is a portable information terminal that includes a mobile telephone, or a portable car navigation device, audio player, or the like.

**[0041]** Additionally, the cermet decorative member of the present embodiment may be suitably used in a ring, an earring, a necklace and the like, and provides a consumer who owns such an accessory with a luxury feel and esthetically pleasing look.

**[0042]** The cermet decorative member of the present embodiment may be suitably used in parts that require decorative value, such as amenity goods, vehicle emblems, and the like.

**[0043]** Next, an example of a manufacturing method of the cermet decorative member of the present embodiment will be described.

**[0044]** First, prescribed quantities of titanium nitride powder having an average particle size of from 10 to 30 μm, titanium carbide powder having an average particle size of from 0.5 to 3.0 μm, nickel powder having an average particle size of from 15 to 25 μm, niobium powder having an average particle size of from 10 to 20 μm, and chromium powder having an average particle size of from 30 to 50 μm are weighed out.

**[0045]** Specifically, from 7.0 to 11.0 mass% of nickel powder, from 1.5 to 6.0 mass% of niobium powder, from 1.0 to 5.0 mass% of chromium powder, and the remainder titanium nitride powder and titanium carbide powder are used as starting raw materials. The weights of titanium nitride powder and titanium carbide powder are preferably chosen to be in the ratio of from 6.5:3.5 to 3:7, and more preferably from 6:4 to 4:6.

**[0046]** Then, among the starting raw materials, the nickel powder, niobium powder, chromium powder, and water or methanol as a solvent are loaded into a mill, where they are mixed and ground (primary mixing and grinding). Grinding only the metal powders for not less than 10 hours leads to the presence of the niobium powder and chromium powder on the periphery of the nickel powder, and at least one of niobium and chromium can form a solid solution in nickel. When the duration of primary mixing and grinding is greater than 30 hours, the effect of promoting solid solution formation reaches its plateau, and therefore the duration of primary mixing and grinding for the purpose of promoting solid solution formation is preferably not greater than 30 hours.

**[0047]** When the cermet contains at least one of molybdenum, tungsten, and cobalt, molybdenum powder, tungsten powder, and cobalt powder may be prepared and added during primary mixing and grinding. Furthermore, for a compound including nickel and chromium to be present in the cermet, the duration of primary mixing and grinding may be not less than 30 hours.

**[0048]** Then, after primary mixing and grinding, the titanium nitride powder and titanium carbide powder are introduced into the mill, and secondary mixing and grinding are performed. A prescribed amount of a binder is then added to obtain a slurry.

**[0049]** The obtained slurry is then spray-dried to form granules, and these granules are molded into a desired shape, such as a round plate, flat plate, annular body, or the like, using a desired molding method, such as dry pressing, cold isostatic pressing, extrusion molding, or the like. If the desired shape is complex, injection molding may also be used as the molding method.

**[0050]** Then, the powder compact is placed in a pressure degreasing furnace and degreased while maintaining a temperature at from 310 to 390°C and a pressure at from 30 to 60 kPa in an inert gas atmosphere. The degreased powder compact may then be fired at from 1200 to 1500°C in vacuum of not greater than 1.33 Pa to produce a sintered compact. Furthermore, to achieve the oxygen content of less than 1.0 mass% per 100 mass% of all components constituting the cermet, it may be held at from 400 to 600°C for not less than 50 minutes when increasing the temperature of firing, and then fired at from 1200 to 1500°C. By holding the temperature at from 400 to 600°C for not less than 50 minutes when increasing the temperature, the oxygen and carbon remaining in the degreased compact react to form carbon dioxide gas which escapes from the degreased compact, and the oxygen content can be reduced to less than 1.0 mass%. In order to set the free carbon content to not less than 1.5 mass% and not greater than 2.5 mass% per 100 mass% of all components constituting the cermet, the degreasing conditions may be adjusted. For example, when the temperature is 350°C and the pressure is 45 kPa, the hold time may be from 10 to 20 minutes.

**[0051]** Then, lap processing is performed using, for example, a tin lapping plate while supplying diamond abrasive grains having an average particle size of not greater than 1 μm, and then barrel polishing is performed. In wet barrel polishing, the compact may be tumbled in a rotary barrel polisher for 24 hours using green carborundum (GC) as a medium.

**[0052]** The cermet decorative member of the present embodiment obtained in the above manner contains a crystal phase including titanium carbonitride and a bonding phase including nickel, niobium, and chromium. The lattice constant of the nickel is not less than 3.54 Å, and it can exhibit a gold color tone with little color variation. Furthermore, the watch, mobile terminal, and accessory obtained using the cermet decorative member of the present embodiment has sufficient mechanical strength for practical use, and can also provide a consumer with a luxury feel and an esthetically pleasing look.

**[0053]** Hereinafter, examples of the present invention will be specifically described. However, the present embodiment is not limited to these examples.

## Example 1

**[0054]** First, titanium nitride powder having an average particle size of 20 μm, titanium carbide powder having an average particle size of 1.0 μm, nickel powder having an average particle size of 20 μm, niobium powder having an average particle size of 15 μm, and chromium powder having an average particle size of 40 μm were weighed out. Thus, a nickel content is 10 mass%, a niobium content is 5.0 mass%, and a chromium content is 3 mass% in the cermet. Note that the ratio of titanium nitride powder to titanium carbide powder was 6:4.

**[0055]** Then, the nickel powder, niobium powder, chromium powder, and water or methanol as a solvent were loaded into a mill, where primary mixing and grinding were performed for the time shown in Table 1.

**[0056]** Next, the titanium nitride powder and titanium carbide powder were loaded into the mill, and secondary mixing and grinding were performed. A prescribed amount of binder was then added to obtain a slurry. Note that for Sample No. 1, primary mixing and grinding were not performed, and only secondary mixing and grinding were performed.

**[0057]** Then, the obtained slurry was spray-dried to form granules, and using these granules, a powder compact was obtained by dry compression molding.

**[0058]** Then, the powder compact was placed in a pressure degreasing furnace and degreased while maintaining a temperature at 350°C and a pressure at 45 kPa in an inert gas atmosphere, and the degreased powder compact was then fired at a temperature of 1500°C in vacuum of not greater than 1.33 Pa to obtain a sintered compact.

**[0059]** Each of the samples was measured using XRD (D8 ADVANCE, manufactured by Bruker AXS GmbH), and the presence of a titanium carbonitride crystal phase was verified. Note that the presence of a titanium nitride crystal phase was also verified for Sample No. 1. The lattice constant of the nickel was also verified by XRD.

**[0060]** Furthermore, when each of the samples was measured using ICP, it was verified that the contents of nickel, niobium, and chromium were as expected from what they were weighed out.

**[0061]** Then, lapping was performed on each of the samples using a tin lapping plate while supplying diamond abrasive grains having an average particle size of not greater than 1 μm, to produce a lapped surface, of which the arithmetic mean roughness Ra on the roughness curve was not greater than 0.03 μm. Then, using a spectrophotometric colorimeter (CM-5, manufactured by Konica Minolta Inc.), the values of lightness of the color L* and psychometric chroma coordinates a* and b* in the CIE 1976 L*a*b* color space were measured according to JIS Z 8722-2000 for three locations in each sample. Note that, as measurement conditions, SCI (specular component included) conditions were used, a CIE standard light source D65 was used as a light source, the illumination receiving mode was di: 8°·de: 8° (diffuse illumination·8° direction reception), and the measurement diameter was 3 mm.

**[0062]** Using the obtained values of L*, a*, and b*, color variation was determined by the formula $\Delta E = [(AL^*)^2 + (Aa^*)^2 + (\Delta b^*)^2]^{1/2}$ .The results are shown in Table 1.

[Table 1]

| Sample No. | Primary mixing and grinding (h) | Lattice constant of nickel (Å) | Color variation ΔE |
|---|---|---|---|
| 1 | 0 | 3.525 | 0.4 |
| 2 | 5 | 3.530 | 0.3 |
| 3 | 10 | 3.540 | 0.2 |
| 4 | 20 | 3.580 | 0.15 |
| 5 | 30 | 3.600 | 0.12 |
| 6 | 40 | 3.600 | 0.12 |

**[0063]** From Table 1, Sample Nos. 3 to 6 have a smaller value of ΔE than Sample Nos. 1 and 2, and it was found that in a cermet containing a crystal phase including titanium carbonitride and a bonding phase containing nickel, niobium, and chromium, a nickel lattice constant of not less than 3.54 Å results in a gold color tone with little color variation. Sample 1-6 is not part of the invention.

Example 2

**[0064]** Cermets having the compositions shown in Table 2 were produced, and color tone was measured and monitor evaluation was conducted. Note that the production method was the same as that used in producing Sample No. 4 of Example 1, except that the components were weighed out to achieve the compositions shown in Table 2. Note that Sample No. 8 was a sample produced under the same conditions as Sample No. 4.

**[0065]** Each of the samples was measured using XRD (D8 ADVANCE, manufactured by Bruker AXS GmbH), and the presence of a titanium carbonitride crystal phase was verified. The lattice constant of titanium carbonitride was also verified. Additionally, each of the samples was measured using ICP, and the contents of nickel, niobium, and chromium were determined.

**[0066]** Then, the values of lightness of the color L* and psychometric chroma coordinates a* and b* in the CIE 1976 L*a*b* color space were determined by performing processing and measurement by the same methods as Example 1.

**[0067]** Then, for each of the samples, five men and five women in each age group of twenties, thirties, forties, and fifties, for a total of 40 monitors, who expressed interest in a purple-tinged gold color, were surveyed by questionnaire in regard to two aspects: luxury feel and esthetically pleasing look. Each sample was evaluated as "A" in the case where the proportion of monitors responding "yes" to both items was not less than 80%, and "B" in the case of one item. Results are shown in Table 2.

[Table 2]

| Sample No. | TiN: TiC | Nickel (mass%) | Niobium (mass%) | Chromium (mass%) | Lattice constant of titanium carbonitride (Å) | L* | a* | b* | Monitor evaluation |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 6.5: 3 | 11 | 6 | 1 | 4.26 | 62 | 5 | 6 | B |
| 8 | 6:4 | 10 | 5 | 2 | 4.27 | 64 | 4 | 5 | A |

(continued)

| Sample No. | TiN: TiC | Nickel (mass%) | Niobium (mass%) | Chromium (mass%) | Lattice constant of titanium carbonitride (Å) | L* | a* | b* | Monitor evaluation |
|---|---|---|---|---|---|---|---|---|---|
| 9 | 5:5 | 9 | 4 | 3 | 4.29 | 66 | 2 | 3 | A |
| 10 | 4:6 | 8 | 2.5 | 4 | 4.30 | 68 | 1 | 1 | A |
| 11 | 3:7 | 7 | 1.5 | 5 | 4.31 | 69 | 0 | 0 | B |

**[0068]** From Table 2, good monitor evaluations were obtained for Sample Nos. 8 to 10, and it was found that due to the lattice constant of the crystal phase including titanium carbonitride being not less than 4.27 Å and not greater than 4.30 Å, the lightness of the color L* in CIE 1976 L*a*b* color space was not less than 64 and not greater than 68, a* was not less than 1 and not greater than 4, b* was not less than 1 and not greater than 5, and decorative quality was superior. Samples 7-11 are not part of the invention.

Example 3

**[0069]** Molybdenum powder, tungsten powder, and cobalt powder were prepared, and samples were produced by reducing titanium carbide powder by 1 mass% in the starting raw material composition of Sample No. 4 of Example 1 and adding an equivalent amount of molybdenum powder, tungsten powder, or cobalt powder to each sample. Other than the starting raw material composition, the samples were prepared by the same method as Sample No. 4 of Example 1. For comparison, Sample No. 4 of Example 1 was also prepared.

**[0070]** The relative density of the obtained samples was then verified. Note that for relative density, the apparent density of a titanium nitride sintered compact was determined according to JIS R 1634-1998, and relative density was determined by dividing this apparent density by the theoretical density of the titanium nitride sintered compact. As a result, it was found that the each of the samples, to which molybdenum powder, tungsten powder, or cobalt powder was added, had a higher relative density than Sample No. 4, and that it is possible to reduce the firing temperature by including at least one type selected from the group consisting of molybdenum, tungsten, and cobalt in the titanium nitride sintered compact. It was also found that a decrease in shape processability due to abnormal grain growth of titanium carbonitride can be suppressed by reducing the firing temperature.

Example 4

**[0071]** Samples were produced with varying time to hold the temperature at 400 to 600°C when increasing the temperature of firing, and color variation was verified. First, the production method was the same as that of Sample No. 4 of Example 1, except for the hold time. For one sample, the hold time at 400 to 600°C was 25 minutes when increasing the temperature of firing, and for another sample, it was 50 minutes.

**[0072]** When oxygen content was measured using an oxygen analyzer (TCH-600, manufactured by LECO Corporation), the oxygen content of the one sample was 2% and $\Delta E$ was 0.2%. In contrast, the oxygen content of the other sample was 0.9% and $\Delta E$ was 0.15. As a result, it was found that color variation can be further reduced by having an oxygen content of less than 1.0 mass% per 100 mass% of all components constituting the cermet.

Example 5

**[0073]** Sample Nos. 12 to 16 were obtained by the same method as Sample No. 4 of Example 1 except that the hold time in degreasing during firing was varied. Note that Sample No. 14 is a sample produced under the same conditions as Sample No. 4.

**[0074]** Then, each of the samples was ground, and the free carbon content was determined by measurement using a carbon analyzer (RC-612, manufactured by LECO Corporation). Note that the content was determined from a calibration curve created using a standard sample (calcium carbonate), and the validity of the calibration curve was confirmed by measuring silicon carbide powder of known free carbon content.

**[0075]** Grinding force was also verified using each of the samples. As the equipment, a flat surface grinder (SGE-515E2T, manufactured by Nagase Integrex Co., Ltd.) equipped with a wheel (SDC400N75B25-5, manufactured by Asahi Diamond Industrial Co., Ltd.) was used. As processing conditions, the rotation speed was 2000 $min^{-1}$, the incision amount was 0.005 mm/pass, and the grinding amount was 1200 V ($mm^3$). Grinding force after 200 passes was measured using a stationary dynamometer (9257B, manufactured by Kistler Group), and samples were ranked from the lowest grinding force value as an evaluation of ease of grinding. Furthermore, prior to processing of each sample, using a truing block made from copper, truing and dressing were performed in each of the samples at a rotation speed of 1500 $\text{min}^{-1}$ with an incision amount of 0.005 mm/pass, and then processing was performed.

**[0076]** Test pieces conforming to JIS R 1601-2008 were produced under the same conditions as when producing each of the samples. Three-point bending strength was measured, and the pieces were ranked from the highest value.

**[0077]** Results are shown in Table 3.

[Table 3]

| Sample No. | Degreasing hold time (min) | Free carbon (mass%) | Grinding force rank | Three-point bending strength rank |
|---|---|---|---|---|
| 12 | 25 | 1.3 | 5 | 1 |
| 13 | 20 | 1.5 | 4 | 2 |
| 14 | 15 | 2.0 | 3 | 3 |
| 15 | 10 | 2.5 | 2 | 4 |
| 16 | 5 | 2.7 | 1 | 5 |

**[0078]** From Table 3 it was found that, due to the fact that the free carbon content was not less than 1.5 mass% and not greater than 2.5 mass% per 100 mass% of all components constituting the cermet, the shape processing time for making the desired shape could be reduced while mechanical characteristics as a decorative member were maintained. The samples 12-16 are not part of the invention.

Reference Signs List

**[0079]**

| | |
|---|---|
| 10 | Watch case |
| 11 | Recessed portion |
| 12 | Lug portion |
| 13 | Bottom portion |
| 14 | Torso portion |
| 20 | Center piece |
| 21 | Through-hole |
| 30 | Outer piece |
| 31 | Pin hole |
| 40 | Pin |
| 50 | Watchband |

## Claims

**1.** A cermet decorative member comprising a sintered compact cermet,
the sintered compact cermet comprising:

a crystal phase containing titanium carbonitride; and
a bonding phase containing at least one metal,
wherein the bonding phase comprises:

nickel as a primary component, having a lattice constant of 3.54 Å or more, determined using an X-ray diffractometer;
niobium; and
chromium,
wherein the titanium carbonitride crystal phase has a lattice constant of 4.27 Å or more and 4.30 Å or less, determined using an X-ray diffractometer;
wherein a content of oxygen is less than 1.0 mass% per 100 mass% of all components constituting;

wherein a content of free carbon is not less than 1.5 mass% and not greater than 2.5 mass% per 100 mass% of all components in the cermet;
wherein nickel is present in an amount from 7.0 to 11.0 mass%, niobium is present in an amount from 1.5 to 6.0 mass%, chromium is present in an amount from 1.0 to 5.0 mass%, and the remainder is titanium carbonitride per 100 mass% of all components that constitute the cermet;
wherein the cermet contains at least one of molybdenum, tungsten and cobalt; and
wherein molybdenum is present in an amount from 0.5 to 2.0 mass%, tungsten is present in an amount from 0.05 to 0.4 mass%, and cobalt is present in an amount from 0.02 to 0.2 mass%, per 100 mass% of all components constituting the cermet.

**2.** A watch comprising the cermet decorative member according to claim 1.

**3.** A mobile terminal comprising the cermet decorative member according to claim 1.

**4.** An accessory comprising the cermet decorative member according to claim 1.

## Patentansprüche

**1.** Ein Cermet-Zierelement, aufweisend ein Sinterkörper-Cermet,
wobei das Sinterkörper-Cermet aufweist:

eine Kristallphase, die Titancarbonitrid enthält, und
eine Bindephase, die mindestens ein Metall enthält,
wobei die Bindephase aufweist:

Nickel als eine Hauptkomponente, mit einer Gitterkonstante von 3,54 Å oder mehr, bestimmt mittels eines Röntgendiffraktometers,
Niob und
Chrom,
wobei die Titancarbonitrid-Kristallphase eine Gitterkonstante von 4,27 Å oder mehr und 4,30 Å oder weniger hat, bestimmt mittels eines Röntgendiffraktometers,
wobei ein Gehalt an Sauerstoff weniger als 1,0 Masse-% pro 100 Masse-% aller bildenden Komponenten ist,
wobei ein Gehalt an freiem Kohlenstoff nicht kleiner als 1,5 Masse-% und nicht größer als 2,5 Masse-% pro 100 Masse-% aller Komponenten im Cermet ist,
wobei Nickel in einer Menge von 7,0 bis 11,0 Masse-% vorhanden ist, Niob in einer Menge von 1,5 bis 6,0 Masse-% vorhanden ist, Chrom in einer Menge von 1,0 bis 5,0 Masse-% vorhanden ist, und der Rest Titancarbonitrid ist, pro 100 Masse-% aller Komponenten, die das Cermet bilden,
wobei das Cermet mindestens eines von Molybdän, Wolfram und Cobalt enthält, und
wobei Molybdän in einer Menge von 0,5 bis 2,0 Masse-% vorhanden ist, Wolfram in einer Menge von 0,05 bis 0,4 Masse-% vorhanden ist, und Cobalt in einer Menge von 0,02 Masse-% bis 0,2 Masse-% vorhanden ist, pro 100 Masse-% aller Komponenten, die das Cermet bilden.

**2.** Eine Uhr, aufweisend das Cermet-Zierelement gemäß Anspruch 1.

**3.** Ein mobiles Endgerät, aufweisend das Cermet-Zierelement gemäß Anspruch 1.

**4.** Ein Zubehörteil, aufweisend das Cermet-Zierelement gemäß Anspruch 1.

## Revendications

**1.** Un élément décoratif en cermet, comprenant un compact fritté en cermet,
le compact fritté en cermet comprenant :

une phase cristalline contenant de carbonitrure de titane, et
une phase de liaison contenant au moins un métal,
dans lequel la phase de liaison comprend :

du nickel comme composant principal, présentant une constante de réseau de 3,54 Å ou plus, déterminée en utilisant un diffractomètre à rayons X,
du niobium et
du chrome,
dans lequel la phase cristalline de carbonitrure de titane présente une constante de réseau de 4,27 Å ou plus et 4,30 Å ou moins, déterminée en utilisant un diffractomètre à rayons X,
dans lequel une teneur en oxygène est inférieure à 1,0 % en masse par 100 % en masse de tous les composants constitutifs,
dans lequel une teneur en carbone libre n'est ni inférieure à 1,5 % en masse ni supérieure à 2,5 % en masse par 100 % en masse de tous les composants dans le cermet,
dans lequel le nickel est présent en une quantité de 7,0 à 11,0 % en masse, le niobium est présent en une quantité de 1,5 à 6,0 % en masse, le chrome est présent en une quantité de 1,0 à 5,0 % en masse, et le reste est le carbonitrure de titane par 100 % en masse de tous les composants qui constituent le cermet,
dans lequel le cermet comprend au moins un parmi le molybdène, le tungstène et le cobalt, et
dans lequel le molybdène est présent en une quantité de 0,5 à 2,0 % en masse, le tungstène est présent en une quantité de 0,05 à 0,4 % en masse, et le cobalt est présent en une quantité de 0,02 à 0,2 % en masse, par 100 % en masse de tous les composants constituant le cermet.

**2.** Une montre comprenant l'élément décoratif en cermet selon la revendication 1.

**3.** Un terminal mobile comprenant l'élément décoratif en cermet selon la revendication 1.

**4.** Un accessoire comprenant l'élément décoratif en cermet selon la revendication 1.

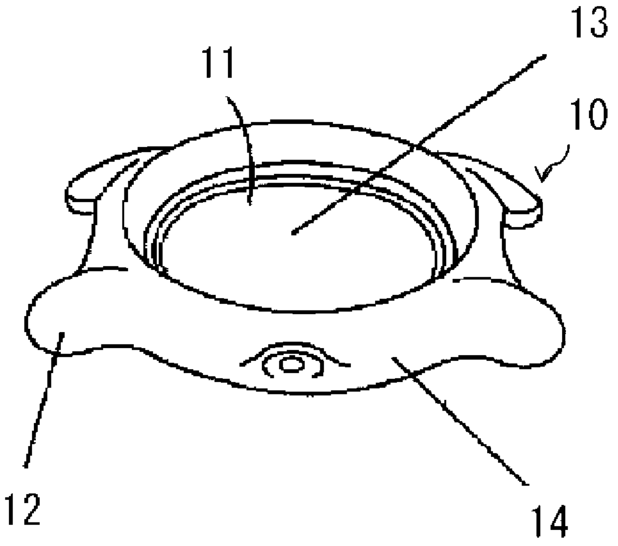

FIG. 1A

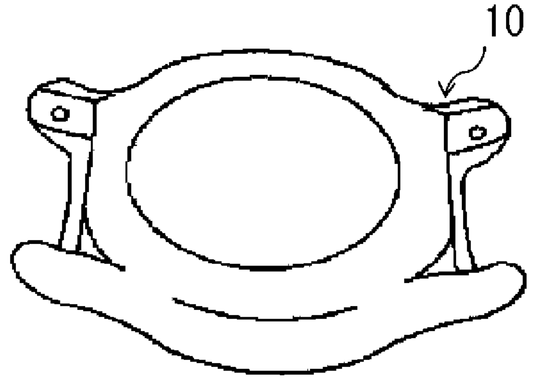

FIG. 1B

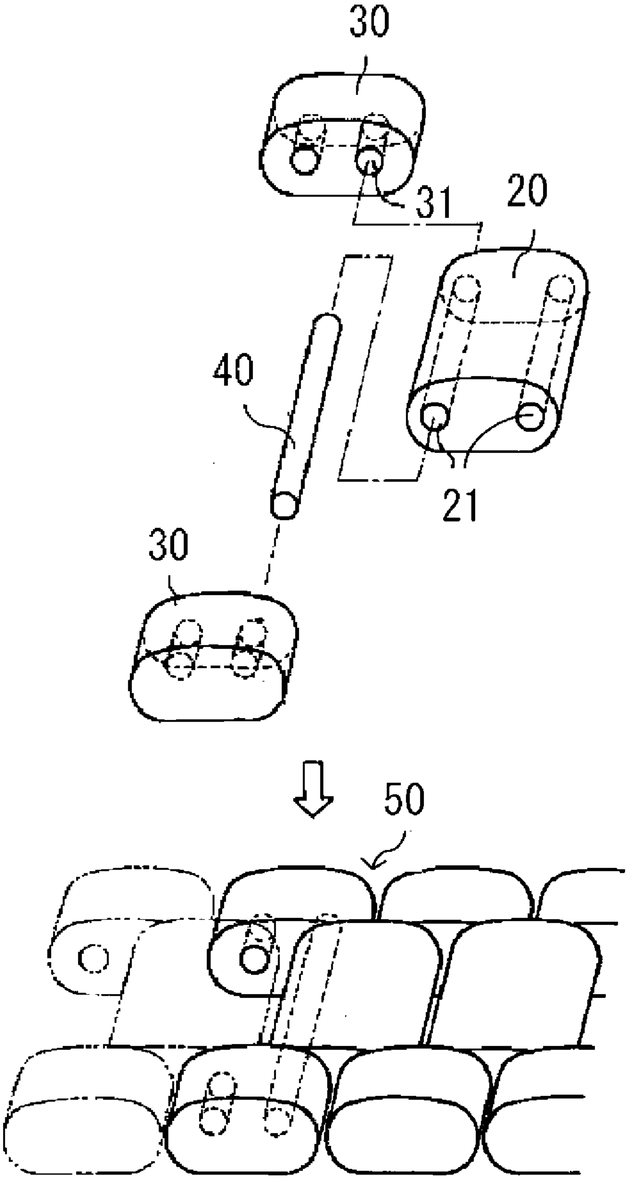

FIG. 2

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- WO 2009069549 A **[0004]**
- WO 2009145146 A **[0005]**
- EP 2298948 A1 **[0006]**
- EP 2568055 A1 **[0007]**
- JP 2011130894 A **[0008]**