# United States Patent [19]

**Kasai et al.**

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[54] **HARD WATCH CASE COMPRISING TIN, T, AND AT LEAST ONE OF MN, AL AND V**


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[73] Assignee: **Kabushiki Kaisha Suwa Seikosha,** Tokyo, Japan



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**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 110,959, Jan. 29, 1971, abandoned.

[30] **Foreign Application Priority Data**

Jan. 30, 1970 Japan ..... 45-7675

[52] **U.S. Cl.** ..... **29/182.5,** 58/88 R, 75/205, 161/213

[51] **Int. Cl.** ..... **C22c 1/04,** G04b 37/00, C22c 1/05, C22c 29/00

[58] **Field of Search** ..... 29/182.5, 182.3; 75/205; 58/88 R; 117/129; 161/213



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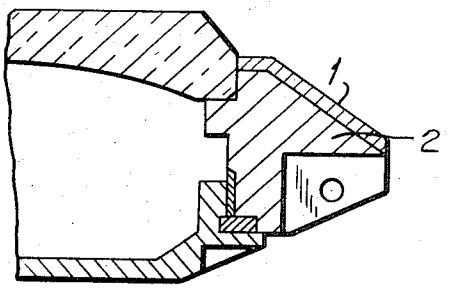


[57] **ABSTRACT**

A watch case resistant to mechanical defacement and corrosion having an external pressed and sintered component at least a part of which comprises TiN with Ti in combination with at least one material selected from the group consisting of Mn, Al, and V as metallic binders.


**10 Claims, 4 Drawing Figures**

FIG. 1



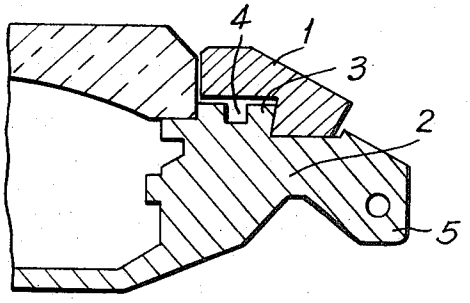
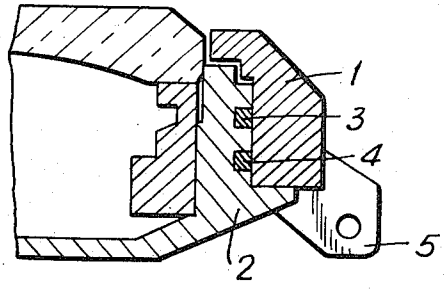




FIG. 2

FIG. 3



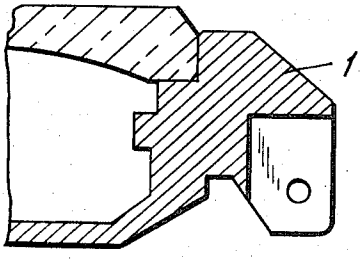




FIG. 4

# HARD WATCH CASE COMPRISING TIN, T, AND AT LEAST ONE OF MN, AL AND V

## CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our application Ser. No. 110,959, filed: Jan. 29, 1971, now abandoned; the priority of said application Ser. No. 110,959 is claimed, and a certified copy of the Japanese application of which said Ser. No. 110,959, is based, is in said application.

## BACKGROUND OF THE INVENTION

In the mass production of conventional watch cases the materials generally used are gold, gold alloy and stainless steel. All of these materials have a low surface hardness (Vickers hardness, Hv, 200 maximum) so that they are easily scratched or abraded by contact with hard metals or concrete and the original high polish of the surface lasts for only a limited time. Also the range of color available with these metals is either the yellow of the gold or the gray of the stainless steel. In addition, gold and gold alloys have high specific gravity as is shown in the Table I below so that where the watch case is large, it can be annoying to the wearer.

## SUMMARY OF THE INVENTION

Hitherto, nitrides have been used only as refractory materials in the form of bricks, boards and crucibles. Such materials are extremely hard, heat and corrosion resistant; in the case of silicon nitride the material has a beautiful light-green color. Moreover, the range of colors can be extended by choice of various binding metals. In addition to being harder than the conventional metals now used, nitrides are available which are much lighter than gold or gold alloys and substantially lighter than stainless steel and some of the carbides which have been used for watch cases. The weight of a watch case made of nitrides can then be substantially lower than the weight of conventional cases, thereby decreasing the burden to the wearer.

TABLE I

Characteristics of Various Materials For a Watch Case

| Materials | Specific Gravity (g/cc) | Hardness (Knoop) | Color |
|---|---|---|---|
| WC | 15.8 | 1880 | Black |
| TiC | 4.9 | 2460 | Black |
| $Si_3N_4$ | 3.18 | 1800 | Faint Green |
| AlN | 3.26 | 1225 | Ash |
| TiN | 5.4 | 1770 | Gold and White |
| ZrN | 7.3 | 1510 | Black and White |
| 18-8 Stainless Steel | 7.9 | 200 | Gray |
| Au | 19.3 | 50 | Yellow |

Of the above materials TiN is particularly suitable for use as the principal constituent of a watch case composition, since it can be varied in color by choice of suitable binder metals, and since compositions containing TiN as herein disclosed have high hardness and high tensile strength and can be sintered at convenient temperatures.

In order to prepare a nitride watch case, a quantity of a metallic powder to serve as a binder is added to powdered nitride, and the mixture is pulverized and mixed in a wet condition in a ball mill for about 100 hours. The powder is then dried in vacuo and lubricants



are added. The mixture is formed into a watch case at a pressure 2 ton/cm$^2$. It is given a preliminary sintering in a vacuum furnace at a pressure of $1 \times 10^{-1}$ to $7 \times 10^{-2}$ mm Hg at a temperature of about 850° C. for about an hour. The watch case is given a final sintering in a vacuum furnace at a pressure preferably of $7 \times 10^{-2}$ to $9 \times 10^{-2}$ mm Hg at a temperature of 1,400° to 1,540° C. for an hour. The lower pressure limit is, of course, not critical. The product is sufficiently hard so that it can be polished only with a diamond wheel.

Accordingly an object of the present invention is to provide a watch case which is resistant to mechanical defacement and to corrosion.

Another object of the invention to provide a watch case which is lighter than conventional watch cases.

Still another object of the invention to provide a watch case with a wide range of colors.

Yet another object of the invention to provide an attractive watch case at reduced cost.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

The invention accordingly comprises the features of construction, combinations of elements, and arrangement of parts which will be exemplified in the constructions hereinafter set forth, and the scope of the invention will be indicated in the claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional view of a watch case the outer surface of which is protected by a nitride layer;

FIG. 2 is a sectional view of a watch case in which the bezel is made of a nitride in accordance with the present invention;

FIG. 3 is a sectional view of a watch case in which a peripheral ring and a lug are made of a nitride composition in accordance with the present invention; and

FIG. 4 is a sectional view of a watch case in which the entire case body and cover are made of nitride in accordance with the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

To prepare a watch case in accordance with the present invention, binder metals including Ti and at least one of Mn, V and Al powders having a particle diameter of 2–3 microns are added to powdered TiN. The powders are pulverized and mixed wet in a ball mill with hard balls for about 100 hours. They are then dried in vacuo and a lubricant, preferably of the paraffin group, necessary for forming is added. The powder is formed into a watch case at a pressure of 2 ton/cm$^2$ and then given a preliminary sintering in a vacuum furnace at a pressure of $1 \times 10^{-1}$ to $7 \times 10^{-2}$ mm Hg at a temperature of 850° C. for an hour. The watch case is given a final sintering in a vacuum furnace at a pressure of $7 \times 10^{-2}$ to $9 \times 10^{-2}$ mm Hg at a temperature of 1,400° to 1,540° C. for an hour. In the process, allowance is made for the fact that the watch case will contract during the final sintering. The product is extremely hard and a diamond wheel is used for the polishing. The resultant surface color varies from that of white gold to that of 18K gold and the surface is lustrous, resembling a jewel. The Vickers hardness is 1,020 to 1,132 and the material cannot be scratched by a knife, a razor, or file or broken glass. In addition, the material is not corroded either by artificial perspiration

or by sea water and consequently the lustrous appearance is essentially permanent. Such a watch case is much lighter than a conventional case made of stainless steel, gold or a gold alloy and is also lighter than cases which are chiefly composed of carbide and contain substantial quantities of heavy metal binders such as nickel, cobalt or molybdenum.

Table II lists a number of compositions based on TiN as the refractory constituent. In each case Ti, together with at least one of Mn, Al and V is used as the binder. The TiN concentration can vary from about 50 percent to about 95 percent by weight. Preferred ranges for the binder metals are as follows:

| | | | |
|---|---|---|---|
| Mn | 0.5 | to | 10% |
| Al | 0.1 | to | 8% |
| V | 0.1 | to | 10% |
| Ti | — | Balance. | |

At TiN concentrations below about 50 percent, the hardness decreases, while at concentrations above 95 percent the tensile strength decreases. For Mn concentrations below 0.5 percent no effect is noted, while at above 10 percent both the color and the hardness are degraded. For Al and V, concentrations below 0.1 percent show no effect, while above about 8 percent for Al and 10 percent for V, color tone, luster and hardness are adversely affected. Titanium in the examples of Table II is shown as lying between 3 and 35 percent. Actually, titanium is used to bring the total weight up to 100 percent after the concentrations of the other constituents are selected.

In making the selection of a composition, the first consideration is usually the color tone desired. Table II makes it possible to choose a composition which will yield the desired properties. Another consideration may be the sintering temperature. As would be expected, the higher the TiN content, the higher the temperature required for proper sintering. The tensile strength also correlates directly with the TiN content.

TABLE II

| Example | TiN | Ti | Mn | Al | V | Sintering Temp °C | Color Tone | Hardness Hv | Tensile Strength kg/mm² |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 60 | 32 | 8 | | | 1450 | white gold | 1226 | 55 |
| 2 | 87 | 11 | 2 | | | 1520 | 18K gold | 1150 | 70 |
| 3 | 85 | 10 | | 5 | | 1540 | gold | 1115 | 62 |
| 4 | 50 | 35 | 10 | 5 | | 1500 | silver yellow | 1290 | 53 |
| 5 | 55 | 33 | 7 | 5 | | 1400 | silver yellow | 1310 | 48 |
| 6 | 87 | 9 | 2 | 2 | | 1520 | light gold | 1087 | 68 |
| 7 | 87 | 11 | 1 | 1 | | 1520 | 18K gold | 1132 | 72 |
| 8 | 86 | 9 | 3 | | 2 | 1520 | light gold | 1018 | 70 |
| 9 | 95 | 3 | 0.5 | | 1.5 | 1520 | white gold | 1020 | 70 |
| 10 | 75 | 10 | | 5 | 10 | 1500 | white gold | 1048 | 60 |
| 11 | 83.5 | 8 | | 0.5 | 8 | 1530 | gold | 1090 | 58 |
| 12 | 87 | 9 | 2 | 1 | 1 | 1520 | reddish gold | 1058 | 70 |

Note: The sintering time for all of the compositions listed is 1 hour, but, in general, the sintering time is not crucial.

In general, the higher the tensile strength, the lower the hardness, which is surprising.

Where these titanium nitride compositions are to be used in combination with stainless steel, the design must take account of the fact that the compositions are extremely hard and show little deformability. FIG. 1 shows a stainless steel watch case in which a hard layer 1 of nitride is superimposed upon the stainless steel case 2. The nitride layer 1 is attached to the stainless steel by the cement.

FIG. 2 shows a stainless steel watch case in which the bezel 1 engages the stainless steel 2 at the snap-ring 3. Since the bezel of nitride can not be substantially deformed, provision must be made for the stainless steel snap-ring to deform. This provision is made through the formation of the groove 4 in the stainless steel body 2. The lug 5, here, is part of the stainless steel body.

In the watch case shown in FIG. 3, the outer case body 1 and the lug 5 are both made of a nitride composition. The outer case body 1 is attached to the inner body 2 by means of cement inserted into the grooves 3 and 4.

In the watch case shown in FIG. 4 the entire case body including the back cover is made of the nitride composition. Such a watch case is resistant to scratching on all of its surfaces.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in the above constructions without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A watch case resistant to mechanical defacement and corrosion, having an external pressed and sintered component comprising TiN, Ti and at least one binder metal selected from the group consisting of Mn, Al and V, the percentage by weight of TiN being from 50 to 95, of Mn being 0.5 to 10, of Al being 0.1 to 8 and of V being 0.1 to 10 with Ti constituting the remainder.

2. The watch case as defined in claim 1 wherein the percentages by weight of TiN, Ti, and Mn are respectively 87, 11 and 2.

3. The watch case as defined in claim 1 wherein the percentages by weight of TiN, Ti, Mn and Al are respectively 87, 11, 1 and 1.

4. The watch case as defined in claim 1 wherein the percentages by weight of TiN, Ti, Al and V are respectively 75, 10, 5 and 10.

5. The watch case as defined in claim 1 wherein the percentages by weight of TiN, Ti, Mn, Al and V are respectively 87, 9, 2, 1 and 1.

6. A watch case as defined in claim 1 having a stainless steel body covered at least in part by said pressed and sintered component.

7. A watch case as defined in claim 6 wherein said pressed and sintered component engages said stainless steel body mechanically.



8. A watch case as defined in claim 6 wherein said pressed and sintered component is attached to said stainless steel body by cement.

9. A watch case as defined in claim 6 wherein said pressed and sintered component is a bezel.

10. A watch case as defined in claim 1 wherein said pressed and sintered component comprises the entire watch case body.

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