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(54) METAL-CONTAINING ARTICLES OF JEWELLERY

(71) We, MARCEL VILLAT, of Muhlenmattweg 1109, Oberentfelden, Aargau, Switzerland, and HANS ULRICH KLINGENBERG, of St. Niklaus, Merzlingen, Bern, Switzerland, both Swiss citizens, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention broadly relates to a new and improved use of hard metals, especially metal boride-containing compositions. More specifically, this invention relates to a metal-containing article of jewellery, and preferably, an article of jewellery which periodically comes into contact with the human body, secretions from the skin and/or organic products. Examples of such articles of jewellery include rings, ear-rings, chains, pendants hanging from chains or necklaces, brooches, cufflinks, arm bands, arm rings, outer parts of watches including watch bands and casings.

The so-called sintered carbides have been widely used in the jewellery industry because they are almost as hard as diamonds. About 95% of the sintered carbides employed in the jewellery industry include the hard carbide powders of tungsten, titanium, molybdenum and tantalum, as well as mixed carbides. These metallic carbide powders are retained or bonded together by a metallic binder, such as cobalt or nickel.

Other metals including iron, chromium, copper, silver, or alloys containing these metals have also been employed as binders for the metallic carbides. These sintered carbides are products of powder metallurgy processes and are basically manufactured by pressing the fine particles of powder of the constituents and thereafter subjecting the pressed article to heat for the purpose of attaining a solid or fixed bond.

Articles of jewellery such as rings, brooches, or external watch components have been completely or partially formed

from sintered carbides in the past. These articles of jewellery exhibit a good metallic lustre and retain a scratch-free surface for a long period of time. However, a serious drawback exists in the use of sintered carbides in jewellery. Due to the presence of moisture and other deleterious impurities in the atmosphere, as well as smoke, exposure to various household products, and various organic products including secretions of the skin, jewellery containing sintered carbides tends to lose its lustre over a period of time and in addition, to exhibit traces of corrosion which usually appear in the form of very unattractive spots or speckling on the surface of the jewellery.

Another drawback to the use of sintered carbides in jewellery is the relatively expensive, complicated double-sintering technique which is generally required in the preparation of sintered carbide-containing jewellery.

Accordingly, it is a primary object of the present invention to provide an improved metal-containing article of jewellery which does not exhibit the drawbacks of the prior art structures noted above.

Another, more specific object of the present invention relates to the provision of an article of jewellery which is comparable in hardness to sintered carbides and unexpectedly exhibits a greater degree of chemical resistance than articles of jewellery formed from sintered carbides when they are exposed to moisture and other deleterious impurities in the atmosphere as well as organic products including secretions of the skin, smoke, and household products.

It has now been found that these objects can be fulfilled by the use of other metallic compounds when a particular metal binding composition is employed in combination therewith.

According to the present invention there is provided a metal-containing article of jewellery formed from a pseudo-alloy consisting of (a) 5—50% by weight of a metal

binder of which at least 30% by weight is at least one of Ni, Cr, Ag and Au, the remaining 70% or less being one or more of the elements Cu, Fe, Mn, Co, Sn, Mo, Sb, Bi, an alloy of any of said metals, or B, said metal binder having dispersed therein (b) 95—50% by weight of at least one metal boride of a metal from groups IVA, VA and VIA of the Periodic Table according to Mendeleef alone or admixed with at least one silicide, nitride and/or carbide of at least one of said metals.

Suitable finely divided borides useful in this invention include the borides of titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten. Particularly preferred are the borides of titanium, zirconium, chromium and tungsten. Mixtures of these borides can also be used, as well as mixed crystals.

The finely divided dispersion phase can contain silicides, nitrides and/or carbides of these sub-group metals in the form of a mixture with the boride or the borides or as mixed crystals. Thus, the finely divided dispersion can contain at least one compound represented by the formula:



wherein M is a metal from group IVA, group VA, or group VIA of the Periodic Table of Elements. A is selected from the group consisting of silicon, nitrogen, and carbon; x is equal to 4 when A is a silicon or carbon, and x is equal to 3 when A is nitrogen; y equals the valence of the metallic ion M.

The amount of binder metal which is employed in the compositions of this invention is largely dependent upon the particular properties to be possessed by the article of jewellery. Generally, the hardness of the article increases with a decreasing quantity or proportion of metal binder which results in an increase in the brittleness of the article. Where relatively noble or precious metals are employed in the metal binder phase, such as copper, silver and gold, the corrosion resistance of the article of jewellery also increases so that relatively greater quantities of metal binder can be employed. The minimum amount of the metal binder employed in the articles of jewellery is 5% by weight of the total article of jewellery.

The remainder of the metal binder material which accounts at maximum for 70% of the metal binder mixture can include various optional elements. These elements are iron, manganese, cobalt, copper, tin, molybdenum, antimony and bismuth. These metals can be present in the metal binder composition by themselves, as mixtures or as alloys thereof. The proportions of copper, tin, antimony, molybdenum and bis-

muth generally amount to half, or 50% by weight of the aforementioned metal binder composition or matrix. The particular type and quantity of the metal or metal mixture employed, depends upon the desired strength, toughness, workability or machinability, corrosion resistance, surface hardness, colour, embellishment or beautification, desired in the article of jewellery. Boron can also be present in amounts of up to one half of the remainder (at most 70%) of the metal binder material or matrix in order to increase the toughness, appearance and luster of the article of jewellery without reducing the corrosion resistance thereof.

As a result of the addition of the above-mentioned copper, tin, antimony, molybdenum and/or bismuth to the compositions, it is also possible to reduce the sintering temperature and impregnating temperature during the fabrication of the articles of jewellery or of raw workpieces therefor, in accordance with the protective or inert gas-, vacuum-, or protective salt-impregnation technique. In so doing, these metals can be sintered together with the at least 30% by weight of gold, silver, chromium and/or nickel and the borides in the form of a powder. It is also possible that these metals can serve as a melt for the impregnation or imbuing of a skeleton body of the borides.

The use of the specified metallic borides in accordance with this invention, produces additional advantages. For example, it is possible easily to produce formed or moulded bodies which do not possess any simple geometric shape — which is the general rule with articles of jewellery — from metal borides in accordance with simple powder metallurgical techniques. Thus, for instance, it is possible to use the convenient impregnation technique in which no dimensional change of the formed or moulded article occurs.

In order to fabricate formed bodies from metal carbides, it is generally necessary to employ the expensive, complicated double-sintering technique, which with borides can be dispensed with. However this technique may be used with good results to prepare the present articles. Furthermore, pressure sintering also results in faultless products which are practically free from pores.

It is well known that the metal boride materials used in this invention are more brittle than materials containing metal carbides. Thus, the metals borides are regarded as having a lower compressive strength and impact strength than the metallic carbides. It is for these reasons that the metallic borides utilized in connection with this invention have not been used up to now as extensively as the metallic carbide

materials. In addition, the materials used in the articles of jewellery of this invention, have not been known to be previously used in the jewellery industry. However, it has been found, as disclosed herein, that the metal borides when admixed with the metal binder compositions of this invention, enable articles of jewellery to be formed which unexpectedly possess satisfactory compressive- and impact strength properties. These values far exceed those values for the noble metals and precious stones or gems.

The use of the finely divided metal borides in the finely divided phase results in the formation of articles of jewellery which possess a softer and warmer color when compared with the harder coloration of the hard metal or sintered carbides. In addition, the articles of jewellery which are prepared in accordance with this invention also exhibit a very pleasant lustre which, under comparable corrosion conditions (e.g., atmospheric influences, bodily secretions) remains for a much longer period of time than with the sintered carbides. Formation of spots or speckling such as that which occurs during the corrosion of sintered carbides could not be observed.

In order to explain more fully the invention, there will now be given a number of examples. They are limited to the description of the materials inasmuch as the production thereof as well as the working into articles of jewellery is well known to those skilled in the art.

EXAMPLE 1

The material contains as the finely divided or fine particle dispersion phase 90% by weight of CrB_2 and as binder metal phase 10% by weight of ferrochromium which contains 70% by weight of chromium.

EXAMPLE 2

The material consists of 80% by weight TiB_2 and 10% by weight of nickel and 10% of ferromanganese with 80% by weight of Mn.

EXAMPLE 3

There is used a material of the following composition:

- 70% by weight of mixed crystals formed of 90 at.% TiB_2 and 10 at.% ZrB_2 ;
- 20% by weight of nickel;
- 10% by weight of silver.

EXAMPLE 4

There is used a material possessing the following composition:

- 60% by weight of W_2B_5 ;
- 40% by weight of metal binder composition consisting of:

- 50% by weight of copper
- 25% by weight of silver
- 25% by weight of gold.

EXAMPLE 5

A material possessing the following composition is also employed:

- 50% by weight of mixed crystals formed of 90% at.% TiB_2 and 10 at.% ZrB_2 ;
- 50% by weight of metal binder composition consisting of:

- 60% by weight of nickel
- 24% by weight of copper
- 11% by weight of tin
- 5% by weight of boron.

EXAMPLE 6

There is used a material of the following composition:

- 50% by weight of chromium boride Cr_5B_3
- 50% by weight of metal binder composition consisting of:

- 40% by weight of chromium
- 20% by weight of molybdenum
- 30% by weight of nickel
- 10% by weight of copper.

WHAT WE CLAIM IS:—

1. A metal-containing article of jewellery formed from a pseudo-alloy consisting of (a) 5—50% by weight of a metal binder of which at least 30% by weight is at least one of Ni, Cr, Ag and Au, the remaining 70% or less being one or more of the elements Cu, Fe, Mn, Co, Sn, Mo, Sb, Bi, an alloy of any of said metals, or B, said metal binder having dispersed therein (b) 95—50% by weight of at least one metal boride of a metal from groups IVA, VA and VIA of the Periodic Table according to Mendeleef alone or admixed with at least one silicide, nitride and/or carbide of at least one of said metals.

2. An article of jewellery as claimed in claim 1 in which when the metal binder contains copper, tin, antimony, molybdenum or bismuth these metals comprise substantially 50% of the weight of the metal binder.

3. An article of jewellery as claimed in claim 1 or claim 2 in which when the metal binder contains boron this comprises up to one-half of the weight of said remaining 70% or less of the metal binder.

4. An article of jewellery as claimed in any of the preceding claims in which said metal boride is a boride of titanium, zirconium, chromium or tungsten or is a mixture thereof.

5. An article of jewellery as claimed in

materials. In addition, the materials used in the articles of jewellery of this invention, have not been known to be previously used in the jewellery industry. However, it has been found, as disclosed herein, that the metal borides when admixed with the metal binder compositions of this invention, enable articles of jewellery to be formed which unexpectedly possess satisfactory compressive- and impact strength properties. These values far exceed those values for the noble metals and precious stones or gems.

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In order to explain more fully the invention, there will now be given a number of examples. They are limited to the description of the materials inasmuch as the production thereof as well as the working into articles of jewellery is well known to those skilled in the art.

EXAMPLE 1

The material contains as the finely divided or fine particle dispersion phase 90% by weight of CrB_2 and as binder metal phase 10% by weight of ferrochromium which contains 70% by weight of chromium.

EXAMPLE 2

The material consists of 80% by weight TiB_2 and 10% by weight of nickel and 10% of ferromanganese with 80% by weight of Mn.

EXAMPLE 3

There is used a material of the following composition:

70% by weight of mixed crystals formed of 90 at.% TiB_2 and 10 at.% ZrB_2 ;
20% by weight of nickel;
10% by weight of silver.

EXAMPLE 4

There is used a material possessing the following composition:

60% by weight of W_2B_5 ;
40% by weight of metal binder composition consisting of:

50% by weight of copper
25% by weight of silver
25% by weight of gold.

EXAMPLE 5

A material possessing the following composition is also employed:

50% by weight of mixed crystals formed of 90% at.% TiB_2 and 10 at.% ZrB_2 ;
50% by weight of metal binder composition consisting of:

60% by weight of nickel
24% by weight of copper
11% by weight of tin
5% by weight of boron.

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There is used a material of the following composition:

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50% by weight of metal binder composition consisting of:

40% by weight of chromium
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30% by weight of nickel
10% by weight of copper.

WHAT WE CLAIM IS:—

1. A metal-containing article of jewellery formed from a pseudo-alloy consisting of (a) 5—50% by weight of a metal binder of which at least 30% by weight is at least one of Ni, Cr, Ag and Au, the remaining 70% or less being one or more of the elements Cu, Fe, Mn, Co, Sn, Mo, Sb, Bi, an alloy of any of said metals, or B, said metal binder having dispersed therein (b) 95—50% by weight of at least one metal boride of a metal from groups IVA, VA and VIA of the Periodic Table according to Mendeleef alone or admixed with at least one silicide, nitride and/or carbide of at least one of said metals.

2. An article of jewellery as claimed in claim 1 in which when the metal binder contains copper, tin, antimony, molybdenum or bismuth these metals comprise substantially 50% of the weight of the metal binder.

3. An article of jewellery as claimed in claim 1 or claim 2 in which when the metal binder contains boron this comprises up to one-half of the weight of said remaining 70% or less of the metal binder.

4. An article of jewellery as claimed in any of the preceding claims in which said metal boride is a boride of titanium, zirconium, chromium or tungsten or is a mixture thereof.

5. An article of jewellery as claimed in



any of the preceding claims which is a ring, armband, ear-ring, arm ring, cufflink, chain or brooch.

- 5 6. An article of jewellery as claimed in any of claims 1—4 which is a watch casing or watch band.

7. An article of jewellery according to

claim 1 and substantially as hereinbefore described with reference to any of the Examples.

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