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TITANIUM AND/OR ZIRCONIUM NITRIDE BASED ARTICLES OF JEWELRY

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ABSTRACT OF THE DISCLOSURE

Fine-grained mixture of 30 to 99 volume percent refractory nitride, 0 to 45 volume percent refractory oxides, borides or carbides, and 0 to 50 volume percent metal are sintered or hot-pressed to form articles of jewelry having low porosity, a golden color, perspiration resistance and a high luster when polished.

BACKGROUND OF THE INVENTION

This invention relates to articles of jewelry which consist essentially of 20 to 100 volume percent refractory nitride, 0 to 70 volume percent refractory oxide, boride or carbides, and 0 to 50 volume percent metal.

Some such compositions are known in the art to possess good hardness and strength as disclosed in U.S. Pats. Nos. 3,409,416, 3,409,417, 3,409,418 and 3,409,419. We have discovered that the compositions of this invention when shaped as articles of jewelry exhibit a number of unusually desirable characteristics. Refractory carbides have been employed in the prior art in making watch cases as disclosed in U.S. Pat. No. 3,242,664. However, refractory carbides have some drawbacks for use in making articles of jewelry. Most refractory carbides have moderate electrical conductivity, a limited resistance to acid-corrosion such as that caused by perspiration, and very high density which makes the articles of jewelry quite heavy. We have discovered that by incorporating substantial amounts of particular nitrides into the composition comprising the articles of jewelry, distinct advantages are obtained. The presence of a nitride of titanium, zirconium, hafnium, niobium, or vanadium increases acid-corrosion resistance and decreases density, resulting in jewelry which resists perspiration corrosion and is light weight. The nitrides also impart a distinct and unusual golden color to the jewelry which is quite pleasing to the eye. In addition to a pleasing appearance, the articles of this invention are unusually scratch-resistant. They can thus be worn for extended periods without being marred or tarnished. The articles of this invention are also very strong and tough and are therefore very durable as compared to many natural and artificial stones and gems used in articles of jewelry. Finally the articles of this invention are quite refractory and thus will not melt or decompose at high temperatures at which conventional metals or alloys would collapse.

SUMMARY

In summary this invention relates to articles of jewelry which comprise a hard polished composition consisting essentially of 20 to 100 volume percent of a nitride of titanium, zirconium, hafnium, niobium, vanadium or their mixtures; 0 to 70 volume percent of a boride or carbide of titanium, zirconium, niobium, tantalum, tungsten, molybdenum, hafnium, vanadium, or chromium, aluminum nitride, alumina, zirconia, silica, titania, magnesia, magnesium aluminate, the rare earth oxides, or their mixtures; and from 0 to 50 volume percent chromium, molybdenum, tungsten, iron, cobalt, nickel, titanium, zirconium, niobium, tantalum, hafnium or their mixtures; said composition having a density of less than 9 grams per cubic centimeter, a porosity of less than 5%, an average grain size of less than 10 microns, a ratio of light reflectance at 555 millimicrons wavelength to that at 450 millimicrons wavelength of between 1.1/1 and 1.6/1, and a resistance to perspiration by corrosion.

Such articles of jewelry are scratch and mar-resistant, strong, tough and very durable and possess a distinctive golden color.

DESCRIPTION OF THE INVENTION

The articles of this invention comprise dense, fine-grained solids containing 20 to 100 volume percent of a refractory nitride or mixture of refractory nitrides selected from among the nitrides of titanium, zirconium, hafnium, niobium, vanadium and their mixtures; 0 to 70 volume percent of an electrically non-conducting component selected from among silica, titania, magnesia, aluminum nitride, alumina, zirconia, magnesium aluminate, the rare earth oxides and their mixtures; 0 to 70 volume percent of an electrically conducting component selected from among the borides and the carbides of titanium, zirconium, niobium, tantalum, tungsten, vanadium, chromium, molybdenum, hafnium and their mixtures; and 0 to 50 volume percent of a metal selected from the group chromium, molybdenum, tungsten, iron, cobalt, nickel, titanium, zirconium, niobium, tantalum or hafnium or mixtures of these metals. These solids are characterized by a density of less than 9 grams per cubic centimeter, low porosity, a small average grain size, a polished surface which is resistant to acid corrosion such as cuased by human perspiration and a ratio of light reflectance at 555 millimicrons wavelength which is from 1.1 to 1.6 times as great as the reflectance at 450 millimicrons wavelength.

COMPONENTS

The articles of this invention comprise dense solids which consists essentially of refractory nitrides TiN, ZrN, HfN, NbN, VN or their mixtures; optionally AlN, Al_2O_3, ZrO_2, $Al_2O_3 \cdot MgO$, SiO_2, TiO_2, MgO, rare earth oxides or their mixtures; optionally borides or carbides of Ti, Zr, Nb, Ta, W, Mo, V, Cr, Hf or their mixtures; and, optionally, Cr, Mo, W, Fe, Co, Ni, Ti, Zr, Nb, Ta or Hf metals or their mixtures.

(a) Nitrides

The essential refractory nitrides suitable for use in this invention are titanium nitride, zirconium nitride, hafnium nitride, niobium nitride, vanadium nitride or their mixtures. These nitrides are used in amounts ranging from 20 to 100 volume percent. Because corrosion resistance, lightness and color are increased with increased amounts of nitrides, it is preferred to use at least 30 volume percent of the nitrides, more preferably 40 volume percent and most preferably 50 volume percent. Because the presence of at least some metal binder is desirable, it is preferred to use no more than 99 volume percent nitride, and to permit for the presence of metal and other components, it is more preferred to use no more than 80 volume percent and it is most preferred to use no more than 75 volume percent nitride. For these reasons it is also preferred to have at least 1 percent metal present when the nitride exceeds 90 percent. Of the nitrides, titanium nitride is the one most preferred for use in the compositions of this invention, and zirconium nitride is next preferred.

The average particle size of the nitrides used should be less than 5 microns and preferably less than about 2 microns. If a starting material is appreciably larger than 5 microns in particle size, it can be pre-ground to reduce its size to that which is acceptable. Of course, the mix-milling of the various components of the preferred compositions, which is carried out to obtain a high degree of homogeneity, will result in some comminution of the nitrides as well as the other starting components.

The nitrides to be used in this invention can be prepared by any conventional method; by nitriding the corresponding finely milled hydrides or metallic elements as described in U.S. Pat. No. 3,409,416; or by a suitable reaction in a molten salt such as described in U.S. Pat. No. 3,409,419. The latter is a preferred method because it results in nitride particles of an average size of less than a micron.

The nitrides can also be formed by the carbon reduction in the presence of nitrogen of the corresponding metal oxides in a manner which is described in the literature. Conventional methods for the preparation of the essential nitrides of this invention are disclosed, for example, in "Nitrides," Chapter VIII of a book entitled "High Temperature Technology," by John M. Blocher, Jr., John Wiley & Sons, N.Y., 1956.

Representative of suitable commercially available nitrides are —325 mesh grade TiN and ZrN powders available from Materials for Industry, Inc., Ambler, Pa., as well as the —325 mesh grade TiN, ZrN and HfN powders and —100 mesh grade NbN and VN powders available from Consolidated Astronautics, Inc., Long Island City, N.Y.

(b) Electrically non-conducting components

The electrically non-conducting components which can be used in the compositions of this invention are aluminum nitride, alumina, zirconia, silica, titania, magnesia, magnesium aluminate ($Al_2O_3 \cdot MgO$), the rare earth oxides and their mixtures. These components are used in amounts ranging from 0 to 70 volume percent. Preferred amounts of these components are 0 to 50 volume percent, and most preferably 0 to 35 volume percent and it is preferred to use aluminum nitride or alumina.

Average particle size of these components should generally be less than about 5 microns and preferably less than about 2 microns. As stated above, the preferred oxide is alumina, and preferably its average particle size is less than 2 microns, most preferably less than 0.5 micron.

If the starting material is appreciably larger than 5 microns in particle size, it can be pre-ground to reduce its size to that which is acceptable. Of course, as mentioned above, the mix-milling of the components carried out to obtain a high degree of homogeneity, will result in some comminution of the components.

The electrically non-conducting components suitable for use in this invention can be in any form so long as they are finely divided. Thus, for example, alumina can be in the form of gamma, eta or alpha alumina or their mixtures. Alpha alumina is a preferred form of alumina because its specific surface area is lower than gamma or eta alumina and is likely to contain less adsorbed water.

The oxides can be prepared by any of the well-known conventional methods or they can be obtained commercially. A suitable commercial alumina is Alcoa Superground Alumina XA-16 with a specific surface area of about 13 square meters per gram. Suitable commercial forms of the other oxides are powders graded —325 mesh such as those available from Materials for Industry, Inc.

The aluminum nitride can be prepared by any of the conventional methods described above for the essential nitrides. Representative of suitable commercially available aluminum nitride is a podwer grade —325 mesh available from Materials for Industry, Inc.

(c) Carbides and borides

The electrically conducting borides and carbides which can be used in the compositions of this invention are the carbides and borides of titanium, tungsten, molybdenum, tantalum, zirconium, vanadium, chromium, hafnium, niobium and their mixtures. These carbides and borides can be used in the compositions of this invention in amounts of 0 to 70 volume percent. Preferred amounts of these components are from 0 to 45 volume percent. It is also preferred to use the carbides of titanium, zirconium or tantalum or titanium diboride, and it is most preferred to use titanium carbide.

The carbides and borides suitable for use in this invention should have an average particle size of less than 5 microns and preferably less than 2 microns. If the starting material has a particle size appreciably larger than 5 microns, it can be pre-ground to reduce its size to 5 microns or less prior to its use. Of course, the mix-milling of the components, as mentioned above, will result in some comminution of the components.

Suitable carbides and borides can be prepared by means well-known to the art or they can be obtained commercially. Representative of suitable commercial carbides and borides are the powders graded —325 mesh such as those available from Materials for Industry, Inc. or from Cerac, Inc.

(d) Metals

The metals which can be used in the compositions of this invention are molybdenum, tungsten, chromium, iron, nickel, cobalt, titanium, zirconium, niobium, tantalum, hafnium and their mixtures with each other.

These metals are used in the compositions of this invention in amounts ranging from 0 to 50 volume percent. It is preferred to have at least 1 and more preferably 5 volume percent of metal present and preferably no more than 20, most preferably no more than 15 volume percent of metal because in this range there is an optimum balance in chip resistance when the pieces are cut and ground, ease of polishing and corrosion resistance.

Of the refractory metals, it is preferred to use molybdenum or tungsten or their mixtures with the iron group metals. Of the iron group metals, nickel is preferred. It is most preferred to use molybdenum or tungsten in combination with Ni.

As stated above, relatively high amounts of metals, up to 50 volume percent, can be used in the compositions of this invention. However, increases in the metal content of the composition should be coupled with corresponding increases in the boride, carbide or oxide content to maintain the corrosion resistance of the compositions. It is believed that molybdenum metal diffuses into the lattice of carbides such as titanium carbide so that if there is sufficient carbide present, there will be little or no free molybdenum metal present, thereby maintaining the high resistance to corrosion.

The metals suitable for use in this invention should have an average particle size of less than 5 microns and preferably less than 2 microns. If the starting powder has a particle size appreciably larger than 5 microns, it can be pre-ground to reduce its size to 5 microns or less prior to its use. Of course, the mix-milling of the components, as described above, will result in some comminution of the components.

Metal powders with the required size and degree of purity can be obtained from commercial sources or they can be prepared by conventional means. A suitable method of preparation is low temperature hydrogen reduction of the corresponding metal oxide, or hydrogen reduction of iron, cobalt or nickel carbonate at a temperature between about 600° C. and 1200° C. Such preparations should be carried out at a temperature as is practical to prevent excessive sintering and agglomeration of the metal being formed.

In the preparation of molybdenum and tungsten from their oxides, it is best to employ a two-stage reduction because of the relative volatility of some of these oxides. The first-stage reduction is carried out below the oxide melting point, such as at 600° C. Then the second-stage reduction is completed at say 900° C.

Metals prepared as described above can be milled in an inert medium to increase their surface area and can then be purified such as with hydrochloric acid. It is desirable to use grinding media, when milling the metal, which is made of the same metal as being ground, the components which are to be mixed with the metal, or very wear-resistant material to avoid introducing impurities by attrition of the media.

Representative of suitable commercially available metals are fine tungsten powder from General Electric, Detroit, Mich., with a nitrogen specific surface area of 2 square meters per gram and fine nickel powder available from International Nickel Co., with a nitrogen specific surface area of 0.5 square meter per gram.

(e) Impurities

The components to be used in the compositions of this invention are preferably quite pure. In particular, it is desired to exclude impurities such as oxygen which would tend to have deleterious effects on the dense compositions.

On the other hand, minor amounts of many impurities can be tolerated with no appreciable loss of properties. Thus the metal can contain small amounts of other metals, although low melting metals like lead should be excluded. Small amounts of other carbides can also be present. Even oxygen can be tolerated in small amounts such as occurs when titanium carbide has been exposed to air, resulting in a few percent of titanium oxy-carbide. However, after the powder components have been milled together and are in a highly reactive state, oxidation, particularly of the metals, occurs easily and should be avoided.

PREPARATION OF THE ARTICLES OF THIS INVENTION

The preparation of interdispersions of the nitrides with the borides, carbides, oxides, or metals if they are used, in the form of a powder, can be carried out in the manner disclosed in U.S. Pat. No. 3,409,416.

The powder interdispersions of the carbides with the oxides, and the metal if they are used, are fabricated by sintering or hot-pressing in the form of a dense solid, also as described in U.S. Pat. No. 3,409,416 as well as U.S. Pat. No. 3,413,392 and copending application Ser. No. 846,525 filed July 31, 1969.

The dense compositions consisting essentially of nitrides and optionally containing oxides, carbides, borides and metal can be shaped into articles of jewelry without the use of any other material. Alternatively the dense compositions can be mounted on a backing such as metal, wood, plastic or cloth, or can be used as a mount for precious or semiprecious stones, gems and minerals. The resulting items of jewelry can be purely decorative, functional or combine function with decoration.

Items of jewelry are so well known and the size, shapes, combinations of materials used and areas of use are so broad that it is impossible and should be uncessary to list all possible types of jewelry for which the compositions of this invention are suitable. The following abbreviated list is merely representative of suitable uses. The compositions of this invention can be used alone or in combination with any structural materials or materials of apparel including metal, wood, glass, minerals, plastics, cloth, paper, leather, precious stones, shells, or synthetic organic or inorganic materials. Combinations can be made for example by brazing, soldering, gluing, cementing, insetting, pegging, and sewing, such jewelry items as the following:

Watch cases
Cuff links
Earrings
Pins
Rings
Tie tacks
Necklaces
Buttons
Clips
Lapel buttons
Bracelets
Monograms
Medals
Shoehorns
Hair ornaments
Belt buckles
Compacts (cosmetic cases)
Charms for charm bracelets
Insignias
Pendants
Cigarette cases
Metal ornaments
Trophies
Bottle openers
Hairpins
Shoe buckles
Pill boxes
Dress or shirt studs
Identification tags
Paper weights

Methods for fabricating such item of jewelry as well as methods for cutting, shaping and polishing the dense compositions will be apparent to those skilled in the art and are more fully described in the examples.

CHARACTERIZATION METHODS

The compositions of this invention are characterized by their visible light reflectance ratio, corrosion resistance to perspiration, high mechanical strength, outstanding toughness and hardness, density, low porosity, small grain size and homogeneity of the interdispersion between components.

Determination of mechanical strength and hardness are made by conventional transverse rupture and Rockwell A methods.

Methods for the determination of porosity, grain size and homogeneity of solid bodies are described in U.S. Pat. No. 3,409,416. The composition of this invention are characterized by a porosity of less than 5% and an average grain size of less than 10 microns. Preferably, compositions of this invention have a porosity less than 1% and an average grain size of less than 2 microns.

Toughness is determined only qualitatively by allowing a finished fabricated object of this invention to freely fall on a hardwood floor from a height of seven feet. The compositions of this invention do not break or chip under the conditions of this test.

The actual density of the compositions can be determined by any recognized method, most simply by weighing in air, and immersed in water, a sample which has been previously measured. The water should be boiled before weighing the sample to remove dissolved air. The density is calculated from the formula

$$\text{density} = \frac{\text{weight in air} \times \text{specific gravity of water}}{\text{weight in air} - \text{weight in water}}$$

The theoretical density for the composition can be calculated on the basis that the volume for a given weight of the composition is equal to the sum of the volumes of the components calculated from the weight of each component divided by its density.

The solid bodies of this invention, as pointed out above, have a density of less than 9 grams per cubic centimeter and since their porosity is generally less than 1%, their actual density will ordinarily exceed 99% of their theoretical density.

One of the characteristics that materials should have, to qualify for their use in pieces of jewelry that are in continuous contact with the skin, such as rings, bracelets and watch cases, is resistance to corrosion by human skin excretions. It is known, for example, that in hot climates even stainless steel watch cases can be corroded completely through in normal use on the wrist. To evaluate this characteristic, a cororsion test using a liquid with the average composition of human perspiration is employed. A solution is prepared with the composition stated to be the average composition of human perspiration in "Normal Values in Clinical Medicine" by F. W. Sunderman and F. Boerner, W. B. Saunders Co., Philadelphia and London, 1949 at page 488. The composition is

	Percent
Water	99.02
Sodium chloride	0.7
Lactic acid	0.1
Acetic acid	0.0096
Propionic acid	0.0062
Caprylic and caproic acid	0.0046
Citric acid	0.004
Ascorbic acid	0.004

No urea or uric acid, included as "traces" in the average composition of human perspiration, are added to the corrosion solution.

The corrosion solution is placed in a beaker in a constant temperature bath at 40° C. and glass stirrers are used to keep the solution stirring gently.

Test specimens used as corrosion coupons are 0.810 inch x 0.500 inch x 0.100 inch in size. They are used as cut with resin-bonded diamond wheels without further grinding or polishing except as needed to conform the coupons to standard size.

Clean test specimens are accurately weighed and measured and then are immersed in boiling dimethylformamide for 4 minutes to ensure no surface contamination. Upon removal from the dimethylformamide the coupons are rinsed with water and acetone, are dried in a vacuum oven, and are transferred directly into the corrosion solution.

At measured intervals the specimens are removed from the corrosion liquid, are rinsed with distilled water and acetone, are dried in a vacuum oven and are then weighed. They are then re-cleaned in boiling dimethylforamide, water and acetone and are dried and returned to the corrosion liquid. Weight loss is calculated per unit of surface area of the specimen for the given intervals of time. The surface of some specimens are examined by optical micrograph before starting the test and at fixed intervals during the test to observe the extent of etching.

The dense compositions of this invention are characterized by a weight loss of less than 5 milligrams per square centimeter after immersion in the above described synthetic perspiration at 40° C. for ten days. This resistance to perspiration corrosion is greater than that of cobalt-bonded tungsten carbide compositions which are currently being used to make scratch resistant watch cases.

The attractive ornamental appearance of the compositions of this invention is one of the most important characteristics for jewelry uses.

The compositions of this invention have a golden appearance due to the deficiency of blue in the reflected spectrum of visible light (about 400 to 700 millimicrons wavelength). The gold color of the compositions of this invention range from yellow gold to bronze gold. The color of these compositions is characterized by measuring their light reflectance ratio at 555 millimicrons and 450 millimicrons. As the yellow or golden component of the compositions increases, so does the IR_{555}/IR_{450} ratio. IR_{555} is the percentage of light intensity of 555 millimicron wavelength reflected and IR_{450} is the percentage of 450 millimicron wavelength reflected light intensity.

Light reflectance measurements of the compositions of this invention are conveniently made by means of the method described below:

A Bausch & Lomb Spectronic 505 spectrophotometer with an integrating sphere attachment is used for the measurements of light reflectance.

The spectra recorded with the Spectronic 505 is obtained using directional illumination and diffuse viewing from the integrated sphere with a trap for the specular reflection.

In the case of diffuse reflection, the integrating sphere collects all the light reflected diffusely (not the direct mirror reflection) from the surface of the sample placed against the opening (called the port) in its side. The integrating sphere is a hollow metal sphere several inches in diameter painted white inside. Illumination of the sample is adjusted at an angle to the normal such that the specularly reflected light (mirror reflection) is trapped in a light trap, and therefore does not contribute to the spectrophotometer readings.

Specimens for light reflectance measurements consist of 1 and ½ inch diameter circular and 1 and ½ inch x 1 and 3/16 inch rectangular hot pressed samples with a flat surface, mounted on 2 inch diameter Bakelite supports flush with the samples. This size of sample is large enough to assure that the surface is within the scope of the instrument's light beam and that the samples fit the port tight enough to prevent light losses.

The surface of the specimen is flat, ground and polished. Polishing is done first with 400-grit and 1000-grit "Vespel" resinoid-bonded diamond wheel on 8 inch diameter wheels at 1175 revolutions per minute and 550 revolutions per minute, respectively. Final finish is obtained by polishing with 6 micron diamond paste using kerosene lubricant and one micron diamond dust impregnated on a rotating cloth disc and lubricated with water.

It is important to make all measurements with samples polished under standard conditions, since the degree of optical smoothness of a surface determines the extent to which incident light is reflected in all directions. A diffusing surface tends to cause reflection equally in all directions. Rough or porous surfaces thus tend to cause reflection in all directions. The smoother the surface the more directional is the reflection.

Measurements made by the instrument are obtained in the form of percent transmission versus light wavelength plots. Compositions of this invention are characterized by smooth light reflectance curves with no peaks, but an increasing reflectance from the blue range of the visible spectrum and a ratio of percent reflectance at 555 millimicrons to that at 450 millimicrons of between 1.1 to 1 and 1.6 to 1.

UTILITY

The jewelry articles comprising compositions of this invention can be used in whatever areas items of jewelry are used, either in a purely decorative sense, or to combine practical utility with decorative advantages. These jewelry compositions have an unusually pleasing metallic luster which because of the presence of the nitrides has an unusual golden tone. While the unusual appearance is due to the presence of the nitride phase, as in most esthetically pleasing effects, the difference in appearance can be observed with the human eye but is difficult to define, to measure or to quantify. Also, as mentioned above, in contrast to conventional metals, including stainless steels, silver or gold, articles of jewelry comprising the compositions of this invention are unusually scratch-resistant. By virtue of their fine grain size and lack of porosity, compositions of this invention can be polished to an unusually high degree and this polish is not scratched, marred on dulled in even the roughest convenventional use when contacted with any conventional materials of construction or items of apparel including metals, glass, concrete, bricks, wood, plastics etc. Also, because of their good corrosion resistance, the compositions of this invention can be worn for long periods in contact with human skin and perspiration without severe tarnishing. The compositions of this invention are stronger and tougher than many materials such as natural or artificial stones or gems or insets used in jewelry, and so they are more durable. Since the materials of this invention are extremely refractory they will not melt or decompose at high temperatures at which conventional metals or alloys would collapse. This unusual combination of properties makes these materials unexpectedly valuable for use in articles of jewelry.

The following examples illustrate the invention. Parts and percentages referred to in the examples are by weight unless otherwise indicated.

EXAMPLE 1

This is an example of a composition containing 50 volume percent of titanium nitride, 20 volume percent of aluminum oxide, 15 volume percent of aluminum nitride, 12 volume percent of tungsten metal and 3 volume percent of nickel metal.

The titanium nitride used is grade —325 mesh powder, available from Materials for Industry, Inc., and has a specific surface area of 1.1 square meters per gram as determined by nitrogen absorption. An electron micrograph of the powder shows dense particles of irregular shapes with sizes between 1 and about 10 microns, with the bulk being between 1 and 2 microns. The carbon content is 0.33 percent and the oxygen content is 0.87 percent. Chemical analysis reveals 76.19 percent of titanium and 18.71 percent of nitrogen.

The alumina used is very finely divided alpha alumina, commercially available as Alcoa Superground Alumina XA–16 and is characterized by X-ray examination as pure alpha alumina. It has a specific surface area of about 13 square meters per gram, which is equivalent to a spherical particle size of about 115 millimicrons. Under an electron microscope this alpha alumina powder appears as aggregates of alumina crystals in the range of 100 to 150 millimicrons in diameter.

The aluminum nitride used is grade —325 mesh powder supplied by Materials for Industry, Inc., and has a specific surface area of 2.3 square meters per gram as measured by nitrogen adsorption. An electron micrograph shows dense particles of very irregular shape Globular particles have diameters ranging between 2 and 12 microns and elongated particles show a width of 1 to 3 microns and a length between 4 and 16 microns. The carbon content is 0.43 percent and the oxygen content is 1.55 percent. The results of chemical analysis show that the powder contains 63.95 percent aluminum and 32.27 percent nitrogen.

The tungsten used is a fine powder available from General Electric. It has a specific surface area of 2.0 square meters per gram and an oxygen content of 0.19 percent. Crystallite size as measured by X-ray diffraction line broadening techniques is 174 millimicrons.

The nickel used is a fine powder, available from International Nickel Co., containing 0.15 percent carbon, 0.07 percent oxygen, and less than 300 p.p.m. iron. The specific surface area of the nickel powder is 0.48 square meters per gram and its X-ray diffraction pattern shows only nickel, which as measured by X-ray line broadening has a crystallite size of 150 millimicrons. Under electron microscope, the powder appears as grains 1 to 5 microns in diameter.

The powders are milled by loading 6000 parts of preconditioned cylindrical cobalt-bonded tungsten carbide inserts, ¼ inch long and ¼ inch in diameter, into a 1.3 liter steel rolling mill about 6 inches in diameter, also charged with 290 parts of "Soltrol" 130 saturated paraffinic hydrocarbon, boiling range 165–210° C. The mill is then charged with 81.45 parts of titanium nitride, 14.66 parts of aluminum nitride, 23.88 parts of the alpha alumina, 69.33 parts of tungsten powder, and 9.08 parts of nickel powder, all as above described.

The mill is then sealed and rotated at 90 revolutions per minute for 5 days. The mill is then opened and the contents emptied while keeping the milling inserts inside. The mill is then rinsed out with "Soltrol" 130 several times until all of the milled solids are removed.

The milled powder is transferred to a vacuum evaporator, and the excess hydrocarbon is decanted off after the suspended material has settled. The wet residual cake is then dried under vacuum with the application of heat until the temperature within the evaporator is between 200° and 300° C., and the pressure is less than about 0.1 millimeter of mercury. Thereafter the powder is handled entirely in the absence of air.

The dry powder is pasesd through a 70 mesh screen in a nitrogen atmosphere, and then stored under nitrogen in sealed plastic containers.

A watch case is prepared from this powder by hot pressing the powder in a graphite mold assembly designed in such a way as to permit hot pressing the powder in the shape of a ring with a round hole of a size into which the encased operating works of a watch can later be press-fitted, the ring serving as a protective and decorative case. The graphite mold consists of a 4 inch long hollow cylinder of graphite with an outside diameter of 2 and ½ inches, the cross-section of the cavity being in the shape of a square with rounded sides. The maximum inside diameter of the cylinder is 2 inches. A hollow piston is placed into the bottom end of the cylindrical mold, the outside diameter of the piston fitting snugly into the inside diameter shape of the mold. The piston has a cylindrical cavity with a 1 and ⅝ inch round cross-section. The end of the piston in the mold is tapered or dished so that the bottom of the ring to be formed from the powder will have a somewhat decorative rounded surface rather than a flat surface. A third hollow cylinder with an outside diameter of about 1 and ⅝ inch and a wall thickness of 1/16 inch fits snugly into the hollow piston and extends up beyond the piston into the mold. Finally, a solid rod fits into the thin-walled inner cylinder to keep it from collapsing during the pressing operation. A weighed portion of 32 parts of powder, calculated to result in a completely dense pressed piece with the proper thickness, is poured into the mold and the mold it tapped so that the powder packs in the cavity formed by the inner wall of the mold, the outer surface of the thin-walled cylindrical spacer and the upper hollowed end of the bottom piston. A second hollow piston is then fitted into the assembly from the top to provide the upper surface for the powder cavity. The entire assembly is placed into a hot press, and is heated quickly to 1000° C. and then to 1800° C. in 10 minutes. The temperature is held at 1800° C. for 2 minutes and then 5000 pounds per square inch pressure is applied through top and bottom solid graphite rams acting on the outer ends of the hollow pistons which protrude from the top and bottom of the mold. Pressure is maintained for 4 minutes and then the heat is cut off and the pressure is released. The mold is then removed immediately from the hot zone and the solid rod spacer is permitted to slide out of the center of the assembly. As the mold cools, the pressed watch case ring contracts more than the graphite. If the solid rod is left in place, the ring would fracture from strains set up. Instead, the shrinking ring compresses the thin-walled graphite cylinder which remains in the hole, and the cylinder cracks instead of the ring. The thin-walled cylinder is used simply to permit initial easy withdrawal of the solid rod which otherwise would be held up by sticking to the ring. After the mold has cooled, the pistons and the ring are removed, by pressure if needed.

The watch case is polished by pressing its faces firmly against rotating diamond impregnated cloth discs. A Buehler, Ltd. machine is used in this operation for polishing the sample. A 400 grit diamond wheel is used at 1175 revolutions per minute in the first polishing step and a 1000 grit diamond at 550 revolutions per minute is used in a second, finishing step.

The finished watch case fabricated in this manner has an attractive golden color.

EXAMPLE 2

The procedure of Example 1 is repeated except that no alumina is used and the rest of the components are used in amounts to give a composition containing 50 volume percent titanium nitride, 30 volume percent aluminum nitride, 18 volume percent tugnsten and 2 volume percent nickel.

The actual amounts of components loaded into the 1.3 liter steel mill are 81.5 parts of titanium nitride, 29.3 parts of AlN, 104 parts of tungsten metal, and 5.4 parts of nickel metal.

A consolidated billet is prepared from the powder by hot pressing the powder in a cylindrical graphite mold having a cavity with a square cross-section of 1 and 1/16 inches x 1 and 1/16 inches and fitted with opposing close-fitting pistons. One piston is held in place in one end of the mold cavity while 40 parts of the powder are dropped into the cavity under nitrogen and evenly distributed by rotating the mold and tapping it lightly on the side. The upper piston is then put in place under hand pressure. The assembled mold and contents are then placed in a vacuum chamber of a vacuum hot press, the mold is held in a vertical position, and the pistons extending above and below are engaged between opposing graphite rams of the press under pressure of about 600 pounds per square inch. Within a period of a minute the mold is raised into the hot zone of the furnace at 1175° C. and at once the furnace temperature is increased while the positions of the rams are locked so as to prevent further movement during the heatup period. The temperature is raised from 1175° to 1800° C. in 10 minutes, and the temperature of the mold is held at 1800° C. for another 2 minutes to ensure uniform heating of the sample. A pressure of 4000 pounds per square inch is then applied through the pistons for four minutes. Immediately after pressing, the mold and contents, still being held between the opposing rams, is moved out of the furnace into a cool zone where the mold and contents are cooled to dull red heat in about 5 minutes.

The mold and contents are then removed from the vacuum furnace and the billet is removed from the mold and sand blasted to remove any adhering carbon.

Density of the finished piece as determined by accurate weighing and measurement of the dimensions is 7.25 grams per cubic centimeter.

The hot pressed composition is nonporous, having no visible porosity under 1000× magnification. This property is important since nonporous materials are more corrosion resistant than porous materials of the same chemical composition. Structurally the composition consists of an extremely fine co-continuous interpenetrating network of titanium nitride, aluminum nitride, and metal alloy.

The specimen is so tough that it does not break or chip when dropped freely to a hardwood floor from a height of 7 feet.

Electron micrographs indicate a very fine grain structure, few grains exceeding 1 or 2 microns in size.

The sample is polished by pressing its faces firmly against rotating diamond impregnated cloth discs. A Beuhler polishing machine is employed for this operation. A 400 grit diamond wheel is used at 1175 revolutions per minute in the first polishing step and a 1000 grit diamond at 550 revolutions per minute is used in a second, finishing step.

The sample polished in this manner has an attractive ornamental appearance with a golden color.

The polished specimen is used for color measurement with a Bausch and Lomb Spectronic 505 spectrophotometer. An eight percent transmittance versus radiation wavelength curve is obtained by diffuse reflection with the integrating sphere.

The reflectance curve obtained rises gradually from a flat portion at about 9.2 percent light reflectance in the violet end of the spectrum between 400 and about 435 millimicrons wavelength, to about 15.5 percent light reflectance in the red end of the visible spectrum. It is this deficiency in blue radiations in the reflected light that gives to the material its distinctive golden appearance. The reflectance at 450 millimicrons is about 9.3 percent and at 555 millimicrons is about 12.3 percent for a ratio of about 1.3/1.

In addition, the low level of light reflectance even in the yellow to red range of the spectrum makes the material look much darker than gold metal when fashioned into a tie bar.

EXAMPLE 3

The procedure of Example 1 is repeated except that the components are used in amounts to give a composition containing 50 volume percent of titanium nitride, 30 volume percent of alumina, 5 volume percent of aluminum nitride, 12 volume percent of tungsten metal and 3 volume percent of nickel metal.

Actual amounts loaded in a 1 gallon steel mill are 299 parts of TiN, 131.5 parts of Al_2O_3, 18 parts of AlN, 255 parts of W, 29.4 parts of Ni, and 1040 parts of "Soltrol" 130.

A square billet prepared as in Example 2, which has a cross-section of 1 and 1/16 inches and about 0.030 inch in thickness, is cut so that specimens 0.80 inch x 0.50 inch x 0.10 inch are obtained from its center portion.

These specimens are used as coupons in corrosion tests in a liquid with the composition of human perspiration as described before. Tests are conducted in a constant temperature bath at 40° C.

The test is carried out by allowing the specimens to stay in the corrosion liquid for a measured length of time, then removing, rinsing with water and acetone, drying in a vacuum oven and weighing. After weighing, the specimens are cleaned in boiling dimethylformamide, rinsed in water and acetone, and when dried, replaced in the corrosion liquid. The above-mentioned procedure is repeated for various lengths of time.

The corrosion liquid is gently stirred during the test and the temperature of the liquid is kept at 40° C. in a controlled constant temperature bath.

After 10 days the average weight loss of the sample is only 1.8 milligrams per square centimeter. Under the same test conditions, commercial cemented tungsten carbide "Carboloy" 90 shows an average weight loss of 25 milligrams per square centimeter.

Optical microscope observations of "Carboloy" 90 samples at 740× magnification, after 10 hours of immersion in the corrosion test solution under the conditions described, show that the surface has been extensively etched. On the other hand, the composition of this example, when observed under the optical microscope after 10 hours in the corrosion test solution, shows only slight surface etching.

A rectangular piece ½ inch x ⅛ inch is cut from the billet, polished and used as an attractive, ornamental golden inset by cementing it with epoxy resin on a tie clip.

EXAMPLE 4

The procedure of Example 1 is repeated except that the components are used in amounts to give a composition containing 50 volume percent zirconium nitride, 30 volume percent aluminum nitride, 18 volume percent molybdenum metal, and 2 volume percent nickel metal.

The zirconium nitride powder used in this preparation is commercially available from Materials for Industry, Inc., Ambler, Pa. The powder is 99.9 percent pure and the particle size is 0.5 to 5 microns.

The aluminum nitride powder and the nickel metal powder used in this preparation are the same as used in Example 1.

The molybdenum powder used is available from the General Electric Co. and has a grain size of less than 325 mesh, a specific surface area as determined by nitrogen adsorption of 0.29 square meter per gram, and an average crystallite size of 354 millimicrons as determined by X-ray diffraction line broadening. An electron micrograph shows the molybdenum powder consists of grains ½ to 3 microns in diameter clustered together in open aggregates. Chemical analysis of the powder reveals 0.2 percent oxygen and no other impurities over 500 p.p.m.

Amounts of the components loaded into the 1.3 liter mill are 106.35 parts of ZrN, 29.35 parts of AlN, 55.07 parts of Mo, and 5.39 parts of Ni.

A watch case prepared with this composition by the procedure of Example 1 has an attractive golden appearance and does not break or chip when allowed to fall freely on a hardwood floor from a height of 7 feet.

EXAMPLE 5

The procedure of Example 1 is repeated, except that the components are used in amounts to give a composition containing 63 volume percent titanium nitride, 30 volume percent alumina, 4 volume percent tungsten metal, and 3 volume percent nickel metal.

The actual amounts loaded in the 1.3 liter steel mill are 101.85 parts of TiN, 35.82 parts of Al_2O_3, 23.15 parts of W, and 8 parts of Ni.

A billet prepared as in Example 2 from this hot pressed composition has a density of 6.15 grams per cubic centimeter, a hardness of 92.2 on the Rockwell A scale and a transverse rupture strength of about 146,000 pounds per square inch. The billet is very tough and can be dropped from a height of 7 feet on a hardwood floor without breaking or chipping.

The billet is cut so that a 9/16 inch x 3/16 inch rectangular piece is removed from the center. The rectangular piece is polished by pressing its face firmly against rotating diamond impregnated cloth discs. A Buehler, Ltd. machine for polishing the sample is used in this operation. A 400 grit diamond wheel is used at 1175 revolutions per minute in the first polishing step and a 1000 grit diamond wheel at 550 revolutions per minute is used in a second, finishing step.

The rectangular piece polished in this manner has a lustrous golden appearance and is used as an ornamental inset by cementing it with epoxy resin to the surface of a metal tie clip.

EXAMPLE 6

The procedure of Example 1 is repeated except that the components are used in amounts to give a composition containing 50 volume percent titanium nitride, 20 volume percent aluminum nitride, and 30 volume percent tungsten metal.

The actual amounts loaded in the 1.3 liter steel mill are 81.44 parts of TiN, 19.55 parts of AlN, and 174.00 parts of W.

A billet prepared as in Example 2 except that the maximum temperature used in the hot pressing operation is 1850° C., has a density of 9.16 grams per cubic centimeter and a transverse rupture strength of about 160,000 pounds per square inch. The billet is very tough and can be dropped on a hardwood floor from a height of 7 feet without breaking or chipping.

The billet of this composition is cut and polished as in Example 5, to obtain a piece one-half inch square, having a metallic golden appearance. The square piece is used as an ornamental inset by cementing it with epoxy resin on a medallion.

EXAMPLE 7

The procedure of Example 1 is repeated, except that the components are used in amounts to give a composition containing 50 volume percent titanium nitride, 45 volume percent titanium diboride, 4.5 volume percent molybdenum metal, and 0.5 volume percent nickel.

The actual amounts loaded in the 1.3 liter steel mill are 83 parts of TiN, 62 parts of TiB_2, 4.5 parts of Mo, and 1.3 parts of Ni.

The titanium diboride powder used in this composition is commercially available from Materials for Industry, Inc. This powder has a nitrogen specific surface area of 1.1 square meters per gram and an oxygen content of 2.32 percent.

A billet prepared as in Example 1 has a density of about 5 grams per cubic centimeter, hardness of about 92.7 on the Rockwell A scale and transverse rupture strength of about 115,000 pounds per square inch.

The billet is cut with a resin-bonded diamond wheel and polished to give two ornamental lustrous golden pieces. The pieces are cemented with epoxy resin to two metal cuff-links.

EXAMPLE 8

The procedure of Example 1 is repeated except that the components are used in amounts to give a composition containing 85 volume percent niobium nitride, 12 volume percent chromium, and 3 volume percent iron.

The nibium nitride powder used in this preparation is commercially available, grade −325 mesh, from Cerac, Inc., Butler, Wis. The powder is 99.5 percent pure.

The chromium metal powder used in this preparation is available from Materials for Industry, Inc. The powder is 99.9 percent pure and the particle size is 1 to 5 microns, as measured by the Fisher Sub-Sieve Sizer. Nitrogen specific surface area is 0.8 square meter per gram, and oxygen content 0.79 percent. An electron micrograph of this powder shows dense particles, generally with smooth edges and only some scalloped edges, and size between 1 and 4 microns. Most of the particles are around 2 microns in size.

The iron metal powder used in this preparation is available from Materials for Industry, Inc., and has a particle size between 1 and 5 microns. The powder is 99.9 percent pure.

The actual amounts of components loaded into the 1.3 liter steel mill are 214.17 parts of NbN, 24.77 parts of Cr, and 7.06 parts of Fe.

A billet is prepared as in Example 2, having a density of about 8.23 grams per cubic centimeter.

The billet of this composition is cut and polished as in Example 5 to obtain ½ inch x ⅛ inch rectangular piece having a golden appearance. The rectangular piece is used as an ornamental inset by cementing it with epoxy resin on a tie clip.

EXAMPLE 9

The procedure of Example 1 is repeated except that the components are used in amounts to give a composition containing 70 volume percent titanium nitride, 27 volume percent tungsten, and 3 volume percent nickel.

The actual amounts of components loaded into the 1.3 liter steel mill are 118.3 parts of TiN, 162 parts of W metal, and 8.32 parts of Ni metal.

A watch case is fabricated as in Example 1, which has an attractive golden color.

EXAMPLE 10

The procedure of Example 1 is repeated except that the components are used in amounts to give a composition containing 50 volume percent titanium nitride, 45 volume percent tantalum carbide, 4.5 volume percent tungsten metal and 0.5 volume percent nickel metal.

The tantalum carbide powder used in this preparation is available from the Adamas Company and has an average particle size of 3 microns. The nitrogen surface area is 0.38 squar meter per gram and oxygen content is 0.07 percent.

The amounts of components loaded into the 1.3 liter steel mill are 81.46 parts of TiN, 197.76 parts of TaC, 25.60 parts of W metal, and 13.03 parts of Ni metal.

A watch case is fabricated as in Example 1, which has a golden color.

We claim:

1. An article of jewelry comprising a hard polished composition consisting essentially of 30 to 99 volume percent of an essential nitride of titanium, zirconium or their mixtures; 0 to 45 volume percent of titanium carbide, tantalum carbide, zirconium carbide, titanium diboride or their mixtures; 0 to 70 volume percent of an electrically

non-conducting component selected from among aluminum nitride, alumina and their mixtures; and 0 to 50 volume percent of a metal selected from among chromium, molybdenum, tungsten, iron, cobalt, nickel, titanium, zirconium, niobium, tantalum, hafnium and their mixtures; said composition having a density of less than 9 grams per cubic centimeter, a porosity of less than 5 percent, an average grain size of less than 10 microns, a resistance to perspiration corrosion and a ratio of light reflectance at 555 milimicrons to that at 450 millimicrons of between 1.1/1 and 1.6/1.

2. An article of claim **1** in which the composition has a porosity of less than 1 percent and an average grain size of less than 2 microns.

3. An article of claim **1** in which the essential nitride is present in amounts of 30 to 99 volume percent and the metal is present in amounts of 1 to 50 volume percent.

4. An article of claim **1** in which the composition consists essentially of 40 to 80 volume percent essential nitride; 0 to 45 volume percent titanium carbide, tantalum carbide, zirconium carbide or titanium diboride; 0 to 50 volume percent electrically nonconducting component and 1 to 20 volume percent of metal.

5. An article of claim **1** in which the ratio of light reflectance is between 1.15/1 and 1.5/1.

6. An article of claim **5** in which the composition consists essentially of 50 to 75 volume percent of an essential nitride selected from among titanium nirtide, zirconium nitride and their mixtures; 0 to 35 volume percent of an electrically non-conducting component selected from among aluminum nitride and alumina; 0 to 45 volume percent of titanium diboride or a carbide selected fdom among titanium carbide, tantalum carbide, zirconium carbide, and their mixtures; and from 5 to 15 volume percent of metal selected from among molybdenum, tungsten and their mixtures with iron, cobalt or nickel.

7. An article of claim **6** wherein the essential nitride is titanium nitride, the boride or carbide is titanium carbide and the metal is selected from among molybdenum, tungsten and their mixtures with nickel.

8. In a watch case the improvement comprising said case having an exposed outer area comprising a hard polished composition consisting essentially of 30 to 80 volume percent of an essential nitride of titanium, zirconium or their mixtures; 0 to 45 volume percent of titanium carbide, tantalum carbide, zirconium carbide, titanium diboride or their mixtures; 0 to 70 volume percent of an electrically non-conducting component selected from among aluminum nitride, alumina and their mixtures; and 0 to 50 volume percent of a metal selected

from among chromium, molybdenum, tungsten, iron, cobalt, nickel, titanium, zirconium, niobium, tantalum, hafnium and their mixtures; said composition having a density of less than 9 grams per cubic centimeter, a porosity of less than 5 percent, an average grain size of less than 10 microns, a resistance to perspiration corrosion and a ratio of light reflectance at 555 millimicrons to that at 450 millimicrons of between 1.1/1 and 1.6/1.

9. A watch case of claim **8** in which the composition has a porosity of less than 1 percent and an average grain size of less than 2 microns.

10. A watch case of claim **8** in which the metal is present in amounts of 1 to 50 volume percent.

11. A watch case of claim **8** in which the composition consists of 40 to 80 volume percent essential nitride; 0 to 50 volume percent electrically non-conducting component and 1 to 20 volume percent of metal.

12. A watch case of claim **8** in which the ratio of light reflectance is between 1.15/1 and 1.5/1.

13. A watch case of claim **12** in which the composition consists essentially of 50 to 75 volume percent of an essential nitride selected from among titanium nitride, zirconium nitride and their mixtures; 0 to 35 volume percent of an electrically non-conducting component selected from among aluminum nitride and alumina; 0 to 45 volume percent of titanium diboride and from 5 to 15 volume percent of metal selected from among molybdenum, tungsten and their mixtures with iron, cobalt or nickel.

14. A watch case of claim **13** in which the essential nitride is titanium nitride and the metal is selected from among molybdenum, tungsten and their mixtures with nickel.

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