

[54] **ALUMINUM OXIDE BASED ARTICLES OF JEWELRY**

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[56]

References Cited

UNITED STATES PATENTS

3,542,529	11/1970	Bergna et al.	75/206
3,242,664	3/1966	Lederry	29/182.8
3,173,785	3/1965	Manganello	75/206

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[57]

ABSTRACT

Fine-grained mixtures of 25 to 75 volume percent refractory aluminum oxide, 25 to 75 volume percent refractory titanium carbide, and 0 to 10 volume percent metal are sintered or hot-pressed to form articles of jewelry having low porosity, a metallic-grey appearance, perspiration resistance and a high luster when polished.

10 Claims, No Drawings

ALUMINUM OXIDE BASED ARTICLES OF JEWELRY

CROSS REFERENCE TO RELATED APPLICATIONS

This case is a continuation-in-part of copending application Ser. No. 878,894, filed Nov. 21, 1969 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to articles of jewelry which consist essentially of 25 to 75 volume percent refractory aluminum oxide, 25 to 75 volume percent refractory titanium carbide, and 0 to 10 volume percent metal.

Some such compositions are known in the art to possess good hardness and strength as disclosed in U.S. Pat. No. 3,542,529 and U.S. Pat. No. 3,493,351. 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 cemented 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 oxides into articles of jewelry distinct advantages are obtained. The presence of alumina reduces electrical conductivity, increases acid-corrosion resistance and decreases density resulting in jewelry which resists perspiration corrosion and is light weight. The alumina also imparts a distinct and unusual 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 and diamonds would be destroyed.

SUMMARY

In summary this invention relates to perspiration corrosion resistant articles of jewelry which comprise a hard polished composition consisting essentially of 25 to 75 volume percent alumina, 25 to 75 volume percent of titanium carbide, and from 0 to 10 volume percent molybdenum, tungsten, niobium and their alloys with each other and with cobalt, nickel, or their mixtures; said composition having a porosity of less than 5 percent, and an average grain size of less than 10 microns.

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

DESCRIPTION OF THE INVENTION

The articles of this invention comprise dense, fine-grained solids containing 25 to 75 volume percent of refractory alumina, 25 to 75 volume percent of titanium carbide, and 0 to 10 volume percent of a metal

selected from the group molybdenum, tungsten, niobium, and their alloys with each other and with cobalt, nickel, or the mixture of these metals. These solids are characterized by low porosity, a small average grain size, and a polished surface which is resistant to acid corrosion such as caused by human perspiration. Compositions where alumina and titanium carbide are each present in the range of 30 to 60 volume percent are preferred. These compositions have the best combination of corrosion resistance and ease of fabrication. The most preferred composition contains 45 volume percent alumina, 45 volume percent titanium carbide and 10 volume percent of a mixture of molybdenum and nickel.

COMPONENTS

The articles of this invention comprise dense solids which consist essentially of refractory Al_2O_3 , titanium carbide, and, optionally, Mo, W, Nb, and their alloys with Co, Ni, or their mixtures.

Average particle size of the titanium carbide and alumina should generally be less than about 5 microns and preferably less than about 2 microns.

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, the mixing of the components, which is carried out to obtain a high degree of homogeneity, will result in some comminution of the components.

The 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 alumina 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 $13 \text{ m}^2/\text{g}$.

Suitable titanium carbide can be prepared by means well-known to the art or they can be obtained commercially. Suitable commercial titanium carbides are the powders graded -325 mesh such as those available from Materials for Industry Inc. or from Cerac Inc. Butler Wisconsin.

The metals which can be used in the compositions of this invention are molybdenum, tungsten, niobium, their alloys with each other and their alloys with nickel, cobalt, and their mixtures.

These metals are used in the compositions of this invention in amounts ranging from 0 to 10 volume percent. Preferred amounts of metal are from 3 to 10 volume percent 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 Mo or W and their alloys with the cobalt or nickel. Of these two metals, Ni is preferred. It is most preferred to use Mo or W in combination with Ni.

As stated above, relatively high amounts of metals, up to 10 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 carbide content to maintain the corrosion resistance of the compositions. It is believed that molybdenum metal diffuses into the lattice of 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, which is carried out to obtain a high degree of homogeneity, 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 cobalt or nickel carbonate at a temperature between about 600°C. and 1200°C. Such preparations should be carried out at as low 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 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, Michigan, with an oxygen content of 0.21 percent, a nitrogen specific surface area of 2 square meters per gram and a crystallite size of 174 millimicrons as measured by X-ray line broadening; and fine nickel powder available from International Nickel Co., with an oxygen content of 0.09 percent, a nitrogen specific surface area of 0.5 square meters per gram and a crystallite size of 150-170 millimicrons as measured by X-ray line broadening.

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 oxycarbide. 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 carbides with the oxides, and the metals if they are used, in the form of a powder can be carried out in the manner disclosed in U.S. Pat. No. 3,542,529.

The powder interdispersions of the titanium carbide with the alumina, 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. 3,542,529 referred to above.

When these compositions are hot pressed, some metal may be squeezed from the billet, thereby changing the composition. This is generally not a serious problem at low metal levels, but may become serious at metal levels above about 7 volume percent, depending somewhat on the titanium carbide content. Thus in order to obtain a finished article containing 7-10 percent by volume metal, it may be necessary to prepare a powder composition containing somewhat higher metal content. Since the amount of excess metal depends on composition and processing conditions, it is most convenient to determine the amount of required excess by trial and error.

The dense compositions consisting essentially of alumina, titanium carbide and optionally 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 and 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 unnecessary 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, inseting, pegging, and sewing, such jewelry items as the following:

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

Methods for fabricating such items 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 corrosion resistance to perspiration, high mechanical strength, outstanding toughness and hardness, 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 compositions of this invention are characterized by a porosity of less than 5 percent and an average grain size of less than 10 microns. Preferably, compositions of this invention have a porosity less than 1 percent 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. A watch case made of the compositions of this invention will 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 the sample both in air and immersed in water. 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 have a density of less than 9 g/cm³ and since their porosity is generally less than 1 percent, their actual density will ordinarily exceed 99 percent 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 normal use on the wrist. To evaluate this characteristic, a corrosion 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

water — 99.02 percent
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 × 0.500 inch × 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 insure 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 dimethylformamide, 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 0.2 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 304 stainless steel, a metal similar to those used commercially to make watch cases and is much greater than cobalt-bonded tungsten carbide compositions which are currently being used to make scratch resistant watch cases.

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 oxides, is somehow softened and made less harsh than either conventional polished metals or polished tungsten carbide. While the unusual appearance is due to the presence of the oxide 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 or dulled in even the roughest conventional use when contacted with any conventional materials of construction or items of apparel including metals, glass, concrete, bricks, wood, plastics etc. Also, because of the unusual corrosion resistance, the compositions of this invention are not tarnished when worn for long periods in contact with human skin and perspi-

ration. These properties render the compositions of this invention particularly well suited for use in watch cases. 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 and diamonds would be destroyed. 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 aluminum oxide, 45 volume percent of titanium carbide and 5 volume percent of metal consisting of about equal parts by volume of molybdenum and nickel.

The alumina, in the form of very finely divided alpha alumina obtained commercially as Alcoa Superground Alumina XA-16 and characterized by X-ray examination as pure alpha alumina, having a specific surface area of about 13 square meters per gram. This surface area 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 titanium carbide powder has a nominal average particle size of 0.6 microns as measured by the Fisher Sub-Sieve Sizer and a specific surface area of about 10 square meters per gram as determined by nitrogen adsorption. This titanium carbide powder "milled to 0.6 microns" grade is commercially available from the Adamas Carbide Corp., Kennilworth, New Jersey. An electron micrograph of a dry mount preparation shows that the titanium carbide grains are between 0.2 and 3 microns in diameter and sometimes are clustered in the form of loose aggregates. The titanium content is about 77.8 percent, the total carbon content is about 18.8 percent, the free carbon is around 0.07 percent, and the oxygen analyses indicate the oxygen content may vary between about 0.8 to 1.6 percent. Analysis by emission spectroscopy shows that Ti is the major component and also gives 0.5 to 2 percent Mo, 0.5 to 2 percent W, 0.5 to 2 percent Ni, 500 to 2500 ppm of Al, 200 to 1000 ppm of Co, 300 to 1500 ppm of Fe, 300 to 1500 ppm of Nb, 200 to 1000 ppm of Cr, 200 to 1000 ppm Si, 100 to 500 ppm of Zr, 50 to 250 ppm of Ca, 50 to 250 ppm of Mn, and 5 to 25 ppm of Mg.

The molybdenum powder is the current standard grade available from Sylvania Electric Products, Inc., Philadelphia, Pa. It has a grain size of less than 325 mesh and a specific surface area as determined by nitrogen adsorption of 0.29 square meters 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 $\frac{1}{2}$ 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 ppm.

The nickel powder is Mond. current standard grade, available from International Nickel Co., New York City, N.Y. The fine nickel powder contains 0.15 percent carbon, 0.07 percent oxygen, and less than 300 ppm iron. The specific surface area of the nickel powder is 0.48 square meters per gram, its X-ray diffraction pattern shows only nickel, which form the line broadening has a crystallite size of 150 millimicrons. Under electron microscope, the powder appears as polycrystalline grains 1 to 5 microns in diameter.

The powders are milled by loading 6000 parts of pre-conditioned cylindrical cobalt-bonded tungsten carbide inserts, $\frac{1}{4}$ inch long and $\frac{1}{4}$ inch in diameter, into a 1.3 liter steel rolling mill about 6 inches in diameter, also charged with 28.7 parts of "Soltrol" 130 saturated paraffinic hydrocarbon, boiling range 175°-208°C. The mill is then charged with 59.5 parts of the alpha alumina, 66.5 parts of the titanium carbide powder, 7.65 parts of the molybdenum powder, and 6.68 parts of the 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 millimeters of mercury. Thereafter the powder is handled entirely in the absence of air.

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

A consolidated billet is prepared from this powder by hot pressing the powder in a cylindrical graphite mold having a cylindrical cavity 1 inch in diameter and fitted with opposing close-fitting pistons. One piston is held in place in one end of the mold cavity while 17.5 parts of the powder is dropped into the cavity under a nitrogen atmosphere 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 100 to 200 pounds per square inch. Within a period of a minute the mold is raised into the hot zone of the furnace at 1000°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 1000° to 1,800°C. in 10 minutes, and the temperature of the mold is held at 1,800°C. for another 2 minutes to ensure uniform heating of the sample. A pressure of 4,000 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 only 4.82 grams per cubic centimeter.

The hot pressed composition is essentially nonporous when examined under 1000 X magnification. This characteristic 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 polycrystalline alpha alumina and of metal bonded titanium carbide.

The composition has a specific resistivity of about 2000 micro-ohm cm. This degree of conductivity indicates continuity of the conducting components of the structure, namely, the metal and titanium carbide. Electron micrographs indicate a very fine grain structure, few grains exceeding 1 or 2 microns in size. The alumina is generally the coarsest phase.

The continuity of the alumina phase is indicated by removing the titanium carbide and metal from the composition by anodic attack for 24 hours in ammonium bifluoride solution. This leaves an electrically non-conducting porous layer on the surface, which to the eye appears to be unchanged, but under electron microscope is shown to be porous due to the removal of the electrically conducting components.

The sample is polished by pressing its faces firmly against rotating diamond impregnated cloth discs. A Beuhler, Ltd. polishing machine is employed for this operation. A 400 grit diamond wheel is used at 1,175 revolutions per minute in the first polishing step and a 1,000 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 dark, hazy, silver color and metallic luster.

Chemical analysis shows, in addition to the alumina, titanium carbide, molybdenum and nickel, the presence of about 2 percent of iron, presumably attrition from the mill, and 4 percent by weight of tungsten presumably present as tungsten carbide and about 0.5 percent of cobalt, both probably picked up from attrition of the milling inserts.

The billet, which is 1 inch in diameter and about 0.30 inch in thickness, is cut so that a piece 0.810×0.500 inch is removed from the center. Corrosion specimens $0.810 \text{ inch} \times 0.500 \text{ inch} \times 0.100 \text{ inch}$ are cut from this center piece. Strips 0.080 inch in thickness are cut from the material remaining to each side of this center piece and are further cut in $0.070 \text{ inch} \times 0.070 \text{ inch}$ square bars for testing transverse rupture strength. Other portions of the billet are used for indentation hardness tests and for insets on metal tie bars. The transverse rupture strength as measured by bending the $0.070 \text{ inch} \times 0.070 \text{ inch}$ test bars on a $9/16 \text{ inch}$ span is about 150,000 pounds per square inch. The hardness is 94.0 on the Rockwell A scale.

Corrosion tests in a liquid with the composition of human perspiration were made at 40°C . using $0.810 \text{ inch} \times 0.500 \text{ inch} \times 0.100 \text{ inch}$ coupons. The composition of human perspiration is given by F.W. Sunderman and F. Boerner on page 488 of "Normal Values in Clinical Medicine", W. B Saunders & Co., Philadelphia and London, 1949 and is as follows:

H_2O — 99.02 percent

NaCl — 0.7 percent

Lactic Acid — 0.1 percent

Acetic Acid — 0.0096 percent

Propionic Acid — 0.0062 percent

Caprylic and caproic acid — 0.0046 percent

Citric acid — 0.004 percent

Ascorbic acid — 0.004 percent

A liquid of this composition is prepared and the accurately measured and weighed, and carefully cleaned corrosion coupons are immersed in liquid. Cleaning of the coupons is done by immersion in boiling dimethylformamide for 5 minutes, followed by rinsing in water and in acetone.

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 again cleaned in boiling dimethylformamide, rinsed in H_2O 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. Specimens of commercial stainless steel 304 and "Carboloy" grade 90 of the same size and cut and cleaned in the same way as the compositions of this invention are also tested, for comparison.

After 10 days, the average weight loss of the composition prepared above is 0.14 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 and stainless steel 304, a metal similar to that used in commercially available watch cases, shows an average weight loss of 0.5 milligrams per square centimeter.

The tests show that the composition prepared above is more resistant to corrosion by human perspiration than stainless steel 304, and far more resistant than commercial "Carboloy" 90.

Optical microscope observations of "Carboloy" 90 samples at 740 X magnification after 10 hours of immersion in the corrosion test solution show that the surface has been extensively etched by the perspiration solution under the conditions of our experiments. 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.

EXAMPLE 2

This is an example of a watch case made with the composition of Example 1.

The procedure of Example 1 is repeated to obtain a dry powder ready to be hot pressed.

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 $2\frac{1}{2}$ 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 hol-

low 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- $\frac{5}{16}$ 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- $\frac{5}{16}$ 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 amount of powder calculated to result in a completely dense pressed piece with the proper thickness is poured into the mold and the mold is 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 and pressed under the conditions described in Example 1. The 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. When the pressing has been completed, the mold is removed 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 had been 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 ring is then polished as described in Example 1, and fitted around the encased watch works.

EXAMPLE 3

This is an example of the use of a composition of Example 1 as an inset for tie clips.

The procedure of Example 1 is repeated to obtain a dense hot pressed billet.

The billet is cut so that a 9/16 inch $\times$ 3/16 inch rectangular piece is removed from the center. The rectangular piece is polished by pressing its faces firmly against rotating diamond impregnated cloth discs. The same Buehler, Ltd. machine employed in Example 1 for polishing the sample is used in this operation. A 400 grit diamond wheel is used at 1,175 revolutions per minute in the first polishing step and a 1,000 grit diamond at 550 revolutions per minute is used in a second, finishing step.

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

The article of jewelry of this example shows an excellent resistance to perspiration corrosion.

EXAMPLE 4

The procedure of Example 1 is repeated except that

only alumina and titanium carbide are used as components, to give a composition containing 40 volume percent alumina and 60 volume percent titanium carbide.

The amounts of components loaded in the 1.3 liter steel mill are 47.7 parts of alumina and 88.9 parts of titanium carbide.

A billet is prepared as in Example 1, except that the maximum temperature used in the hot pressing operation is 1,850°C. The product has a density of 4.85 grams per cubic centimeter, a hardness higher than 94.5 on the Rockwell A scale, and a transverse rupture strength of about 120,000. The billet is dropped on a hard wood floor from a height of 7 feet without breaking or chipping.

The billet is essentially nonporous, when examined under 1,000 $\times$ magnification. The structure of the composition consists of two very fine continuous interpenetrating networks, one of polycrystalline alpha alumina and one of titanium carbide.

The composition has a specific resistivity of 1,000 micro-ohm.cm., indicating continuity of titanium carbide, the conducting component of the structure.

Electron micrographs indicate a very fine grain structure, few grains exceeding 3 or 4 microns in size.

The polished sample has a most attractive ornamental appearance; a hazy or smoky, dark, silvery gray material with metallic luster.

Chemical analysis shows, in addition to the alumina and titanium carbide, the presence of about 0.5 weight percent of iron, presumably attrition from the steel mill, and about 1.1 percent by weight of tungsten, presumably present as tungsten carbide, and about 0.1 percent of cobalt, both of the latter two probably picked up from attrition of the milling inserts.

Corrosion tests in a liquid with the average composition of human perspiration at 40°C. show that this sample is more resistant to corrosion than stainless steel 304 and far more resistant than commercial "Carboly" 90 tungsten carbide.

The billet of this composition is cut and polished as in Example 3, to obtain a piece one-half inch square. The square piece is used as an ornamental insert by cementing it with epoxy resin on a medallion.

EXAMPLE 5

The procedure of Example 1 is repeated except that niobium metal is used instead of molybdenum metal to give a composition containing 50 volume percent alumina, 45 volume percent titanium carbide, 4 volume percent niobium metal, and 1 volume percent nickel.

The niobium metal used in this composition is obtained commercially from Cerac, Inc., as a -325 mesh powder. This powder has a nitrogen specific surface area of 0.2 square meters per gram and electron micrographs reveal that it is composed of dense particles between 2 and 12 microns in diameter, with most particles between 4 and 8 microns in diameter.

The amounts loaded in the 1.3 liter steel mill are 58.5 parts of alumina, 66.5 parts of titanium carbide, 10.28 parts of niobium metal, and 2.66 parts of nickel metal.

A billet prepared as in Example 1 has a density of 5.02 grams per cubic centimeter, a hardness of about 94.0 on the Rockwell A scale and transverse rupture strength of about 155,000 pounds per square inch.

The billet shows an excellent resistance to human perspiration corrosion.

The billet is cut with a resin bonded diamond wheel and polished to give an ornamental piece of attractive metallic-silver appearance. The resultant piece is cemented with epoxy resin to a steel belt buckle.

We claim:

1. A perspiration, corrosion resistant article of jewelry comprising a hard, polished homogeneous interdispersion consisting essentially of 25 to 75 volume percent of alumina, 25 to 75 volume percent of titanium carbide and 0 to 10 volume percent of a metal selected from the group consisting of molybdenum, tungsten, niobium, and their alloys with each other and with cobalt, nickel, or their mixtures; said composition having a porosity of less than 5 percent, and an average grain size of less than 10 microns.

2. An article of claim 1 in which the composition consists essentially of 30 to 60 volume percent alumina, 30 to 60 volume percent of titanium carbide and 3 to 10 volume percent of a metal selected from the group consisting of molybdenum, tungsten, niobium, and their alloys with each other and with cobalt, nickel or their mixtures.

3. 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.

4. An article of claim 2 wherein the metal is a mixture of molybdenum or tungsten with nickel.

5. An article of claim 1 in which the composition consists essentially of 45 volume percent alumina, 45 volume percent titanium carbide and 10 volume per-

cent of a mixture of molybdenum and nickel.

6. A hard, polished, homogeneous interdispersion for the exposed outer area of a watch case consisting essentially of 25 to 75 volume percent of alumina, 25 to 75 volume percent of titanium carbide and 0 to 10 volume percent of molybdenum, tungsten, niobium, and their alloys with each other and with cobalt, nickel, or their mixtures, said composition having a porosity of less than 5 percent, and an average grain size of less than 10 microns.

7. A composition for a watch case of claim 6 in which the composition consists essentially of 30 to 60 volume percent alumina, 30 to 60 volume percent of titanium carbide, and 3 to 10 volume percent of a metal selected from the group consisting of molybdenum, tungsten, niobium, and their alloys with each other and with cobalt, nickel, or their mixtures.

8. A composition for a watch case of claim 6 in which the composition has a porosity of less than 1 percent and an average grain size of less than 2 microns.

9. A composition for a watch case of claim 6 in which the metal is a mixture of molybdenum or tungsten with nickel.

10. A composition for a watch case of claim 6 in which the composition consists essentially of 45 volume percent alumina, 45 volume percent titanium carbide and 10 volume percent of a mixture of molybdenum and nickel.

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