(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 December 2012 (06.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/167008 A1

(51) International Patent Classification:
A44C 27/00 (2006.01)

(21) International Application Number:
PCT/US2012/040356

(22) International Filing Date:
1 June 2012 (01.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/493,249 3 June 2011 (03.06.2011) US

(71) Applicant *(for all designated States except US)*: **FREDERICK GOLDMAN, INC.** [US/US]; 154 W. 14th Street, New York, New York 10011 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **DERRIG, Andrew** [US/US]; 114 Stevenson Street, Lynbrook, New York 11563 (US).

(74) Agent: **BOCK, Joel N.**; SNR DENTON US LLP, P.O. BOX 061080, Wacker Drive Station, Willis Tower, Chicago, Illinois 60606 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: MULTI-COATED METALLIC PRODUCTS AND METHODS OF MAKING THE SAME

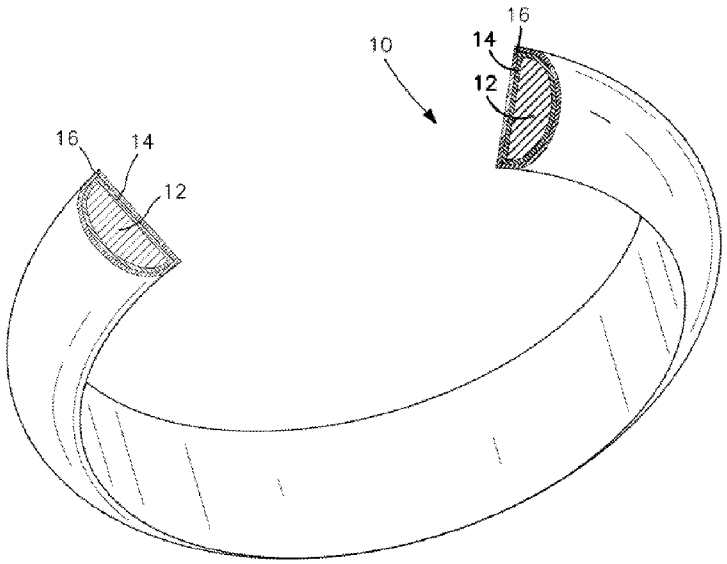

FIG. 1

(57) **Abstract**: In some embodiments the present invention relates to a method for producing a jewelry article or a coated component of a jewelry article, comprising: (a) providing a jewelry article or a coated component of a jewelry article; (b) subjecting the jewelry article or coated component of the jewelry article to a first layering process to obtain a first coated jewelry article or coated component of a jewelry article comprising a first coating; and (c) subjecting the first coated jewelry article or coated component of the jewelry article to a second layering process to obtain a second coated jewelry article or coated component of a jewelry article comprising a second coating.

WO 2012/167008 A1

TITLE OF INVENTION

MULTI-COATED METALLIC PRODUCTS AND METHODS OF MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority to U.S. Provisional Application Serial No. 61/493,249 filed on 03 June 2011, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] Field of the Invention

[0003] The present invention relates generally to coated metal or metallic products and methods for producing such products.

[0004] Background

[0005] The present application generally relates to metal or metallic articles such as jewelry that are coated or plated with metal or metallic coatings.

[0006] Plating is a process where a thin layer of metal is deposited on the surface of a substrate. Metals are plated for various reasons, including for decoration, to harden, to alter conductivity, to inhibit corrosion, to reduce friction, to improve paint adhesion, to improve solderability, to improve wearability, and for radiation shielding. Gemstones can also be plated to provide improved color characteristics. See, *e.g.*, U.S. Patent 5,853,826.

[0007] Processes used in plating include electroplating, physical vapor deposition (PVD) and chemical vapor deposition (CVD). In electroplating, an electrical current is used to reduce cations of a coating material from a solution to coat a conductive substrate with a thin layer of the material. In PVD, a vaporized form of the coating metal is condensed in a vacuum onto the substrate surface. Vaporization and deposition of the coating metal can be effected by a number of methods known in the art, including evaporative deposition, electron beam physical vapor deposition, sputter deposition, cathodic arc deposition, pulsed laser deposition, and plasma-spray deposition. CVD

involves exposing the substrate to a volatile precursor of the coating metal, which reacts or decomposes on the substrate surface.

[0008] While electroplating is the simplest process of plating a metal, electroplating is difficult or impossible where the substrate is a refractory metal such as tungsten, molybdenum, niobium, tantalum or rhenium. In particular, tungsten and tungsten alloys such as tungsten carbide cannot be electroplated. Thus, a tungsten or tungsten alloy article such as an article of jewelry cannot be directly electroplated with, *e.g.*, a layer of a precious metal such as gold, platinum or rhodium. This makes production of plated articles of a tungsten or tungsten alloy substrate difficult to produce. There is thus a need for new methods of making such articles. The present invention addresses that need.

SUMMARY

[0009] In some embodiments, the present invention relates to a method for producing a jewelry article or a coated component of a jewelry article, comprising: (a) providing a jewelry article or a coated component of a jewelry article; (b) subjecting the jewelry article or coated component of the jewelry article to a first layering process to obtain a first coated jewelry article or coated component of a jewelry article comprising a first coating; and (c) subjecting the first coated jewelry article or coated component of the jewelry article to a second layering process to obtain a second coated jewelry article or coated component of a jewelry article comprising a second coating. In further embodiments, the jewelry article or coated component of the jewelry article comprises at least one of tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, 316 stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, tungsten copper, brass, bronze, zinc, tin, German silver, niobium, molybdenum, rhenium, hafnium and combinations and alloys of each of the foregoing. In still further embodiments, the first substrate is tungsten carbide. In additional embodiments, the first coating comprises at least one of a metal,

a material having metallic properties, a metal compound, a metallic compound, a metal alloy, a metal carbide and a metal boride.

[0010] In some embodiments, the jewelry article is a ring, ornamental ring, engagement ring, toe ring, watch, watchcase, watchband, bracelet, necklace, pendant, charm, armlet, brocade, pin, clip, hairclip, fob, ornamental piercing, earring, nose ring, dog tag, amulet, bangle bracelet, cuff bracelet, link bracelet, cuff link, key chain, money clip, cell phone charm, signet ring, class ring, friendship ring or purity ring or a component thereof. In further embodiments, the first coating comprises at least one of titanium diboride (TiB_2), tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, brass, bronze, zinc, tin, German silver, niobium, molybdenum, hafnium, rhenium, chromium, a steel alloy, chromium carbide, zirconium carbide, tantalum carbide, cobalt chrome molybdenum and combinations and alloys of each of the foregoing. In further embodiments, the first coating is chromium. In still further embodiments, the first coating exhibits electrical conductivity. In additional embodiments, the first coating is deposited onto the substrate using vapor deposition, physical vapor deposition (PVD) or chemical vapor deposition (CVD).

[0011] In some embodiments, the second coating comprises at least one of titanium nitride (TiN), titanium(2) nitride (Ti_2N), titanium carbo-nitride (TiCN), titanium-aluminum nitride (TiAlN), titanium-aluminum carbo-nitride (TiAlCN), chromium nitride (CrN), zirconium nitride (ZrN), chromium-titanium nitride (CrTiN), aluminum-titanium nitride (AlTiN), aluminum-titanium-chromium nitride (AlTiCrN), tungsten nitride (WN), titanium diboride (TiB_2), tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, brass, bronze, tungsten copper, zinc, tin, German silver, niobium, molybdenum, hafnium, rhenium, chromium, a steel alloy, gold nitride, silver nitride, aluminum nitride, vanadium nitride, tantalum nitride, chromium carbide, zirconium carbide, tantalum carbide, cobalt chrome molybdenum and combinations and

alloys of each of the foregoing. In further embodiments, the second coating alters the luster of the jewelry article. In still further embodiments, the luster is selected from color change, adamantine, dull, greasy, metallic, pearly, resinous, silky, submetallic, vitreous, waxy, asterism, aventurescence, chatoyancy, and schiller. In additional embodiments, the second coating exhibits electrical conductivity. In some embodiments, the second coating is deposited onto the substrate using electroplating, physical vapor deposition (PVD) or chemical vapor deposition (CVD). In further embodiments, the substrate is capable of being manipulated prior to the first layering process. In still further embodiments, the manipulation is performed using at least one of a CNC machine, a laser, photo lithography, a water jet, a lathe, a tumbler, a drill, a saw, a file, a tool, power tools and hand tools.

[0012] In some embodiments, the present invention relates to a coated jewelry item or a coated component of a jewelry item having a plurality of metal or metallic layers, comprising: a jewelry item or a component of a jewelry item; a first coating comprising a metal, a metal compound, a material having metallic properties or a compound having metallic properties, wherein the first coating is coupled to the jewelry item or the component of the jewelry item; and a second coating comprising a metal, a metal compound, a material having metallic properties or a compound having metallic properties, wherein the second coating is coupled to the first coating, and wherein the jewelry item or the component of the jewelry item, the first coating and the second coating form a surface that is resistant to deformation and wear. In further embodiments, the jewelry item or the component of the jewelry item, the first coating and the second coating form a surface that substantially retains the color of the second coating. In further embodiments, the jewelry item or the component of the jewelry item, comprises at least one of tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, 316 stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, tungsten copper, brass, bronze, zinc, tin, German silver, niobium, molybdenum, rhenium, hafnium and combinations and alloys of each of the foregoing. In still further embodiments, the jewelry item or the

component of the jewelry item comprises tungsten carbide. In additional embodiments, the first coating comprises at least one of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy, a metal carbide and a metal boride. In some embodiments, the first coating exhibits electrical conductivity.

[0013] In some embodiments, the first coating is deposited onto the jewelry item or the component of the jewelry item, using vapor deposition, physical vapor deposition (PVD) or chemical vapor deposition (CVD). In further embodiments, the first coating comprises at least one of titanium diboride (TiB_2), tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, brass, bronze, zinc, tin, German silver, niobium, molybdenum, hafnium, rhenium, chromium, a steel alloy, chromium carbide, zirconium carbide, tantalum carbide, cobalt chrome molybdenum and combinations and alloys of each of the foregoing. In still further embodiments, the second coating comprises at least one of titanium nitride (TiN), titanium(2) nitride (Ti_2N), titanium carbo-nitride (TiCN), titanium-aluminum nitride (TiAlN), titanium-aluminum carbo-nitride (TiAlCN), chromium nitride (CrN), zirconium nitride (ZrN), chromium-titanium nitride (CrTiN), aluminum-titanium nitride (AlTiN), aluminum-titanium-chromium nitride (AlTiCrN), tungsten nitride (WN), titanium diboride (TiB_2), tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, brass, bronze, tungsten copper, zinc, tin, German silver, niobium, molybdenum, hafnium, rhenium, chromium, a steel alloy, gold nitride, silver nitride, aluminum nitride, vanadium nitride, tantalum nitride, chromium carbide, zirconium carbide, tantalum carbide, cobalt chrome molybdenum and combinations and alloys of each of the foregoing. In additional embodiments, the second coating alters the luster of the metallic substance. In some embodiments, the luster is selected from color change, adamantine, dull, greasy, metallic, pearly, resinous, silky, submetallic, vitreous, waxy, asterism, aventurescence, chatoyancy, and schiller. In further embodiments, the second coating

exhibits electrical conductivity. In still further embodiments, the second coating is deposited onto the substrate using electroplating, physical vapor deposition (PVD) or chemical vapor deposition (CVD). In additional embodiments, the first coating is selected from the group consisting of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy, metal carbide and metal boride. In some embodiments, the second coating is selected from the group consisting of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy, metal carbide and metal boride. In further embodiments, the second coating comprises at least one of gold, silver, platinum, palladium, rhodium, ruthenium and an alloy of any of the foregoing. In still further embodiments, the second coating is a galvanic coating.

[0014] In some embodiments, the present invention further comprises washing the coated jewelry article or the coated component of the jewelry article. In further embodiments, the coated jewelry article, coated component of the jewelry article or coated jewelry item exhibits a non-gray color or luster. In other embodiments, the coated jewelry article, coated component of the jewelry article or coated jewelry item substantially retain the color of the second coating. In still further embodiments, the jewelry article, component of the jewelry article or jewelry item comprises at least one of tungsten carbide, chrome, chromium, cobalt chrome or cobalt chromium. In additional embodiments, the coated jewelry article, coated component of the jewelry article or coated jewelry item comprises at least one layer of tungsten carbide, chrome, chromium, cobalt chrome or cobalt chromium. In some embodiments, the coated jewelry article, coated component of the jewelry article or coated jewelry item comprises at least one layer of steel, 316 stainless steel, nickel, nitinol, zirconium, cobalt, chrome, chromium, titanium-zirconium (TiZi), titanium-niobium-zirconium (TiNiZi) and an alloy of any of the foregoing. In further embodiments, the present invention relates to a method for making a jewelry ring comprising a substrate, a first coating of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy, metal carbide and metal boride, and an external metal or metallic coating, the method comprising cutting, pressing, molding, casting, striking, extruding, sintering and/or

shaping the substrate into a ring shape; depositing the first coating onto the substrate; and depositing the external metal or metallic coating onto the first coating.

[0015] A method for making a jewelry ring comprising a substrate, a first coating of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy and a metal carbide, and an external metallic coating is additionally provided. The method comprises cutting, pressing, molding, casting, striking, extruding, sintering and/or shaping the substrate into a ring shape; depositing the first coating onto the substrate; and depositing the external metallic coating onto the first coating.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 shows a ring in accordance with an illustrative embodiment with a transverse cross-sectional cutout.

[0017] FIG. 2 shows a longitudinal cross-section of a ring in accordance with an illustrative embodiment.

[0018] FIG. 3 shows one embodiment of a chrome-steel (chromium-steel) composition of the second coating by component percentage.

[0019] FIG. 4 shows a comparison between the appearance of varying percent compositions of chrome-steel (chromium-steel) alloys in the second coating of rings produced in accordance with the present disclosure, as well as rings essentially comprising tungsten-carbide alloy ("classic TC") or cobalt chrome alloy ("classic cobalt").

[0020] FIG. 5 shows a schematic for producing a coated jewelry article in accordance with an illustrative embodiment.

DETAILED DESCRIPTION

[0021] In a method for making a jewelry ring, according to the present disclosure, the cutting, pressing, molding, casting, striking, extruding, sintering and/or shaping of the substrate can utilize any process known in the art, for example using a vacuum arc furnace, plasma hearth melting, induction skull melting, free smithing, wire electric

discharge machining (EDM), sink EDM, CNC lathe, and/or any polishing or engraving method known. Heat treatments may also be performed to impart desired characteristics to the ring.

[0022] In various embodiments, the first coating is deposited onto the substrate by physical vapor deposition or chemical vapor deposition. In additional embodiments, the external metallic coating is deposited onto the first coating using any known deposition technique, such as, for example, vapor deposition, PVD or CVD. Where a hard surface is desired, for example for an article that is subject to extensive wear, such as a portion of a picture frame, a paperweight, or a portion of a piece of furniture (*e.g.*, an inlay) that may be abraded during use, this process provides a surface that is resistant to deformation and wear.

[0023] The present disclosure describes jewelry articles and coated components of jewelry articles as well as methods for producing the same. The articles and components produced in the context of the present disclosure advantageously comprise at least two coatings each comprising a metal, metal alloy, metalloid or compound exhibiting metallic or metalloid-like properties. In some embodiments, the first coating decreases the deformation and/or physical degradation of the jewelry article and/or coated component of a jewelry article. In some embodiments, the second coating advantageously increases the robustness, hardness and sustainability of the jewelry article and/or coated component of a jewelry article. In the context of the present invention, it is intended that the "hardness" of the jewelry article and/or coated component of a jewelry article may be determined using a standard measure for hardness, including but not limited to the Mohs scale of hardness. See, *e.g.* Gupta, *Chemical Metallurgy*: *Principles and Practice*, Wiley-VCH, 2003.

[0024] The process is shown in FIG. 5. In accordance with the present disclosure, as shown in step 101, the articles and components are first cleaned in a mild detergent solution with the aid of an ultrasonic cleaner to remove all grease and manufacturing residue. The articles and components are then placed in a rack special designed for optimal exposure in a PVD machine. Specifically, the hooks affixed to the rack are designed such that they exhibit minimal contact with the inside surface of the

articles and components to avoid "shading," a defect that occurs when the PVD substrate remains in the same location and the hook used to hold the substrate in covers or occludes that area from proper coverage of the deposition layer. As shown in step 103, the articles and components are next run through a deposition process, such as a PVD or CVD process to deposit a first coating. In some embodiments, the methods of the present disclosure utilize a dual layer PVD process, which uses a multi-target PVD machine that allows for uninterrupted movement from one deposition layer to another without interruption of the vapor deposition cycle, which minimizes the risk of poor adhesion of the deposited film to the substrate. In some embodiments, the first coating is a pure chrome (chromium) deposit applied that measures approximately 0.1 microns in thickness under a vacuum in an inert atmosphere, such as argon gas. As shown in step 105, the first coated articles and components are next run through a second process, either a CVD, PVD or electroplating process, the selection may depend, for example, on the materials used, to deposit the second coating. In some embodiments, the second layer is applied during the second half of the PVD cycle as a cobalt-chrome alloy (cobalt-chromium) deposition layer made up of approximately 60% cobalt, approximately 35% chrome and approximately 5% other compounds, including but not limited to carbon, manganese, silicon, phosphorus, sulfur, molybdenum, nickel and alloys thereof. The second layer is deposited under an inert atmosphere at a thickness of approximately 0.2 microns. As shown in step 107, after deposition of the second coating the coated articles and components are removed from the PVD, CVD or electroplating equipment, and are then may be rinsed and packaged.

[0025] The articles and components produced in accordance with the present disclosure may comprise varying percentages of metals, materials having metallic properties, metal and/or metallic compounds, metal alloys and metal carbides. In some embodiments, as shown in FIG. 3 and FIG. 4, the articles and components may comprise chrome:stainless steel (chromium:stainless steel) ratios including but not limited to 30:70, 60:40, 70:30, 75:25, 80:20 and 90:10. In further embodiments, additional compounds, including but not limited to carbon, manganese, silicon, phosphorus, sulfur, molybdenum, nickel and alloys thereof, may comprise the articles

and components produced in accordance with the present disclosure. For example, a jewelry article comprising a chrome:stainless steel ratio of 90:10 may, in some embodiments, comprise about 0.003% carbon, about 0.2% manganese, about 0.1% silicon, about 0.005% phosphorus, about 0.003% sulfur, about 1.7% chrome (chromium), about 0.25% molybdenum, about 1.2% nickel and about 6.5% iron.

[0026] Described herein are articles having two or more metallic coatings. In various embodiments, the first metallic coating provides a substrate for depositing or electroplating the second, external metallic coating.

[0027] Particularly suitable external metallic coatings for these articles are any material that can be electroplated or vapor deposited onto the first coating. In some embodiments, the external metallic coating comprises a material that imparts an attractive coloration to the article, for example platinum, rhodium, palladium, ruthenium, gold, a gold alloy, silver, a silver alloy, zirconium, tungsten nitride, tungsten carbide, or chrome or one of the materials described above. In particular embodiments, the external metallic coating modifies the luster of the article.

[0028] For example, one specific embodiment of a ring comprises a tungsten carbide substrate, a chromium first coating, and a rhodium external metallic coating.

[0029] The external metallic coating can be any coating appropriate for the metallic article. Where a hard surface is desired, for example for an article that is subject to extensive wear, such as a belt buckle, a picture frame, a paperweight, or a portion of a piece of furniture (*e.g.*, an inlay) that may be abraded during use, the external metallic coating can be a hard material such as TiAlN, TiN, or TiB_2. In other embodiments, the external metallic coating comprises a material that enhances the luster and/or imparts an attractive coloration to the article, including but not limited to titanium nitride (TiN), titanium(2) nitride (Ti_2N), titanium carbo-nitride (TiCN), titanium-aluminum nitride (TiAlN), titanium-aluminum carbo-nitride (TiAlCN), chromium nitride (CrN), zirconium nitride (ZrN), chromium-titanium nitride (CrTiN), aluminum-titanium nitride (AlTiN), aluminum-titanium-chromium nitride (AlTiCrN), tungsten nitride (WN), titanium diboride (TiB_2), tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless

steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, zinc, tin, German silver, niobium, molybdenum, hafnium, rhenium, chromium, a steel alloy, gold nitride, silver nitride, aluminum nitride, vanadium nitride, tantalum nitride, chromium carbide, zirconium carbide, tantalum carbide, cobalt chrome molybdenum and combinations and allows of each of the foregoing.

[0030] FIGS. 1 and 2 provide a transverse cutout (FIG. 1) and a longitudinal cross-section (FIG. 2) of a finger ring 10 in accordance with some embodiments. In these embodiments, the substrate 12 is coated with a first coating 14 and an external metallic coating 16. In the figures, the thicknesses of the first coating 14 and the external metallic coating 16 are not necessarily drawn to scale.

[0031] Definitions

[0032] In the description herein, a number of terms are used. In order to provide a clear and consistent understanding of the specification and claims, the following definitions are provided:

[0033] As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. Additionally, the use of “or” is intended to include “and/or”, unless the context clearly indicates otherwise.

[0034] Electroplating: Refers to the process of moving metal ions in solution via an electrical or conductive field to coat an object. This process is used for the deposition of a material, such as a metal or metal alloy, for imparting a desirable property onto the object, including but not limited to resistance to scratching, corrosivity, chipping and dulling.

[0035] Jewelry: As used herein, “jewelry” refers to personal adornments worn for ornament or utility. Jewelry includes but is in no way limited to rings, ornamental rings, engagement rings, toe rings, watches, watchcases, bracelets, necklaces, chains, pendants, charms, armlets, brocades, pins, clips, hairclips, carved beads, fobs, ornamental piercings, earrings, nose rings, body jewelry, dog tags, amulets, bangle bracelets, cuff bracelets, link bracelets, cuff links, tie clips, tie pins, tie tacks, key chains,

money clips, cell phone charms, cutlerys, writing utensils, pens, charms, signet rings, class rings, friendship rings or purity rings.

[0036] Layering: As used herein, "layering" refers to a process wherein a composition, advantageously a metallic composition, is applied to a substrate optionally comprising zero, one, or more layered composition(s). In some embodiments, layering is performed using a machine or instrument capable of performing a vapor deposition or electroplating process.

[0037] Luster: As used herein, "luster" refers to the way light interacts with the surface and visual appearance of a substance. In some embodiments, the substance is a jewelry article. In further embodiments, the substance is a metallic substance that is optionally capable of being manipulated.

[0038] Manipulable: As used herein, a substance that is "manipulable" is one capable of being patterned, surface modulated, etched, carved, faceted, cut, pressed, molded, cast, stricken, extruded, inlayed, shaped, polished, grinded, scraped, rubbed, sanded, buffed and/or filed. In preferred embodiments, the substance is a substrate for use in the present disclosure.

[0039] Metal Alloy: As used herein, a "metal alloy" is a mixture of two or more metals or of substances with metallic properties. In some embodiments, metal alloys for use in the present disclosure comprise at least one transition metal including but in no way limited to tungsten, cobalt, tungsten, titanium, zirconium, tantalum, aluminum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, nickel, niobium, vanadium, ruthenium, copper, zinc, tin, molybdenum, hafnium and rhenium. In certain embodiments, the metal alloy is selected from a gold alloy, silver alloy, platinum alloy, palladium alloy and iron alloy. In further embodiments, a stainless steel alloy is selected from types 18-8, 304 and 316.

[0040] Metal Carbide: A "metal carbide" is a compound comprising at least one transition metal or substance with metallic properties and carbon or carbon containing chemical group. In certain embodiments, metal carbides for use in the present disclosure include but are in no way limited to tungsten carbide, tungsten-copper carbide, tungsten-silver-copper carbide, titanium carbide, zirconium carbide, niobium

carbide, hafnium carbide, vanadium carbide, tantalum carbide, chromium carbide, aluminum carbide and molybdenum carbide.

[0041] Metal Nitride: A "metal nitride" is a compound comprising at least one transition metal or substance with metallic properties and nitrogen or nitrogen containing chemical group. In some embodiments, metal nitrides for use in the present disclosure include but are in no way limited to titanium nitride, chromium nitride, zirconium nitride, tungsten nitride, gold nitride, silver nitride, aluminum nitride, vanadium nitride, tantalum nitride, aluminum-titanium-nitride, titanium-aluminum-nitride and titanium-carbon-nitride.

[0042] Metal Salt: A "metal salt" is a compound comprising at least one cationic, transition metal or cation with metallic properties and an anion. In some embodiments, metal salts for use in the present disclosure comprise at least one transition metal including but in no way limited to tungsten, cobalt, titanium, zirconium, tantalum, aluminum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, cobalt, chromium, aluminum, vanadium, ruthenium, copper, zinc, tin, nickel, niobium, molybdenum, rhenium and hafnium.

[0043] Metal Sulfide: A "metal sulfide" is a compound comprising at least one transition metal or substance with metallic properties and sulfur or sulfur containing chemical group.

[0044] Polishing: As used herein, "polishing" refers to the process of smoothing and/or increasing the luster of a surface by the application of physical or chemical action or agent to a substance.

[0045] Vapor Deposition: Refers to a general process for the deposition of compounds onto a designated substrate. In preferred embodiments, the use of vapor deposition in the context of the present disclosure refers to chemical vapor deposition (CVD), physical vapor deposition (PVD), plasma enhanced chemical vapor deposition (PECVD), diamond CVD coating, ionized physical vapor deposition (IPVD), sputtering and thermal evaporation. In certain embodiments, vapor deposition is optionally used to add a first and/or a second layer to a substrate used to produce a jewelry article. In preferred embodiments, the first and/or second layer comprises a metal coating comprising one or more of tungsten, cobalt, tungsten, titanium, zirconium, tantalum,

aluminum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, nickel, niobium, vanadium, ruthenium, copper, zinc, tin, hafnium, molybdenum and rhenium. In certain embodiments, the metal alloy is selected from a gold alloy, silver alloy, platinum alloy, palladium alloy and iron alloy. In further embodiments, a stainless steel alloy is selected from types 18-8, 304 and 316.

[0046] Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification or practice of the invention as disclosed herein. It is intended that the specification be considered exemplary only, with the scope and spirit of the invention being indicated by the claims.

[0047] In view of the above, it will be seen that the several advantages of the invention are achieved and other advantages attained.

[0048] As various changes could be made in the above methods and compositions without departing from the scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

[0049] All references cited in this specification are hereby incorporated by reference. The discussion of the references herein is intended merely to summarize the assertions made by the authors and no admission is made that any reference constitutes prior art. Applicants reserve the right to challenge the accuracy and pertinence of the cited references.

REFERENCES

[0050] The following references are incorporated herein by reference in their entireties: U.S. Patent No. 5,021,208; U.S. Patent No. 6,062,045; U.S. Patent No. 6,928,734.

[0051] The following references are also incorporated by reference herein in their entirely: U.S. Patent No. 6,544,315, title “Sintered Jewelry and Decorative Articles”; U.S. Patent No. 6,553,667, titled “Apparatus and Method for Manufacturing Composite Articles Including Wear Resistant Jewelry and Medical and Industrial Devices and

Composites Thereof"; U.S. Patent No. 6,990,736, titled "Methods for Preparing Jewelry Articles Comprising Sintered Tungsten Carbide"; US. Patent No. 6,993,842, titled "Methods and Jewelry Articles Comprising Sintered Tungsten Carbide"; U.S. Patent No. 7,032,314, titled "Methods of Making Tungsten Carbide-Based Annular Jewelry Rings"; U.S. Patent No. 7,076,972, titled "Tungsten Carbide-Based Annular Jewelry Article"; U.S. Application Number 12/141,791, titled "Tungsten Ring Composition"; U.S. Patent No. 7,761,996, titled "Methods of Making Tungsten Carbide-Based Annular Jewelry Rings"; U.S. Patent No. 8,061,033, titled "Methods of Making Tungsten Carbide-Based Annular Jewelry Rings"; U.S. Pat. App. Ser. No. 61/492,197, filed June 1, 2011; U.S. Pat. App. Ser. No. 61/493,283, filed June 3, 2011; U.S. Pat. App. Ser. No. 13/152,226, filed June 2, 2011, titled "Multi-Coated Metallic Articles and Methods of Making Same"; Dobkin *et al*., "Principles of Chemical Vapor Deposition," Springer, New York (2003); and Mahan, "Physical Vapor Deposition of Thin Films," Wiley-Interscience, New York (2000).

CLAIMS

Claim 1. A method for producing a coated jewelry article or a coated component of a jewelry article, comprising:

providing a jewelry article or a component of a jewelry article;

subjecting the jewelry article or the component of the jewelry article to a first layering process to obtain a first coated jewelry article or a first coated component of a jewelry article comprising a first coating; and

subjecting the first coated jewelry article or the first coated component of the jewelry article to a second layering process to obtain the coated jewelry article or coated component of the jewelry article comprising a second coating, wherein the jewelry article or the component of the jewelry article, the first coating and the second coating form a surface that is resistant to deformation and wear.

Claim 2. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the jewelry article or the component of the jewelry article or the substrate comprises at least one of tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, 316 stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, tungsten copper, brass, bronz, zinc, tin, German silver, niobium, molybdenum, rhenium, hafnium and combinations and alloys of each of the foregoing.

Claim 3. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the jewelry article or the component of the jewelry article or the substrate comprises tungsten carbide.

Claim 4. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the first coating comprises at least one of a metal, a material having

metallic properties, a metal compound, a metallic compound, a metal alloy and a metal carbide.

Claim 5. The method of claim 1, wherein the jewelry article or the component of the jewelry article is a ring, ornamental ring, engagement ring, toe ring, watch, watchcase, watchband, bracelet, necklace, pendant, charm, armlet, brocade, pin, clip, hairclip, fob, ornamental piercing, earring, nose ring, dog tag, amulet, bangle bracelet, cuff bracelet, link bracelet, cuff link, key chain, money clip, cell phone charm, signet ring, class ring, friendship ring or purity ring, or a component thereof.

Claim 6. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the first coating comprises at least one of tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, brass, bronze, zinc, tin, German silver, niobium, molybdenum, hafnium, rhenium, chromium, a steel alloy, chromium carbide, zirconium carbide, tantalum carbide, cobalt chrome molybdenum and combinations and alloys of each of the foregoing.

Claim 7. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the first coating comprises chromium.

Claim 8. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the first coating exhibits electrical conductivity.

Claim 9. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the first coating is deposited onto the substrate using physical vapor deposition (PVD) or chemical vapor deposition (CVD).

Claim 10. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating comprises at least one of titanium nitride (TiN), titanium(2) nitride (Ti_2N), titanium carbo-nitride (TiCN), titanium-aluminum nitride (TiAlN), titanium-aluminum carbo-nitride (TiAlCN), chromium nitride (CrN), zirconium nitride (ZrN), chromium-titanium nitride (CrTiN), aluminum-titanium nitride (AlTiN), aluminum-titanium-chromium nitride (AlTiCrN), tungsten nitride (WN), tungsten carbide, cobalt, tungsten, titanium, titanium carbide, zirconium, tantalum, rhodium, gold, silver, platinum, palladium, iridium, iron, stainless steel, cobalt chrome, cobalt chromium, nickel, nitinol, aluminum, aluminum carbide, vanadium, ruthenium, copper, brass, bronze, tungsten copper, zinc, tin, German silver, niobium, molybdenum, hafnium, rhenium, chromium, a steel alloy, gold nitride, silver nitride, aluminum nitride, vanadium nitride, tantalum nitride, chromium carbide, zirconium carbide, tantalum carbide, cobalt chrome molybdenum and combinations and alloys of each of the foregoing.

Claim 11. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating alters the luster of the jewelry article.

Claim 12. The method of claim 11 or jewelry item or component of the jewelry item of claim 11, wherein the luster is selected from color change, adamantine, dull, greasy, metallic, pearly, resinous, silky, submetallic, vitreous, waxy, asterism, aventurescence, chatoyancy, and schiller.

Claim 13. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating exhibits electrical conductivity.

Claim 14. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating is deposited onto the substrate using electroplating, physical vapor deposition (PVD) or chemical vapor deposition (CVD).

Claim 15. The method of claim 1, wherein the jewelry article or the component of the jewelry article is capable of being manipulated prior to the first layering process.

Claim 16. The method of claim 15, wherein the manipulation is performed using at least one of a CNC machine, a laser, photo lithography, a water jet, a lathe, a tumbler, a drill, a saw, a file, power tools and hand tools.

Claim 17. The method of claim 1, wherein a surface is formed, or jewelry item or component of the jewelry item of claim 28, further comprising a surface, that substantially retains the color of the second coating.

Claim 18. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the first coating is selected from the group consisting of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy and a metal carbide.

Claim 19. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating is selected from the group consisting of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy and a metal carbide.

Claim 20. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating comprises at least one of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy and a metal carbide.

Claim 21. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating comprises at least one of gold, silver, platinum, palladium, rhodium, ruthenium and an alloy of any of the foregoing.

Claim 22. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the second coating is a galvanic coating.

Claim 23. The method of claim 1, further comprising:

washing the coated jewelry article or coated component of the jewelry article.

Claim 24. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the jewelry article or coated component of the jewelry article exhibits a non-gray color or luster.

Claim 25. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the jewelry article or coated component of the jewelry article comprises at least one of tungsten carbide, chrome, chromium, cobalt chrome or cobalt chromium.

Claim 26. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the jewelry article or coated component of the jewelry article comprises at least one layer of tungsten carbide, chrome, chromium, cobalt chrome or cobalt chromium.

Claim 27. The method of claim 1 or jewelry item or component of the jewelry item of claim 28, wherein the jewelry article or coated component of the jewelry article comprises at least one layer of steel, 316 stainless steel, nickel, nitinol, zirconium, cobalt, chrome, chromium, titanium-zirconium (TiZi), titanium-niobium-zirconium (TiNiZi) and an alloy of any of the foregoing.

Claim 28. A jewelry item or a component of a jewelry item having a plurality of metal or metallic layers, comprising:

a substrate;

a first coating comprising a metal, a metal compound, a material having metallic properties or a compound having metallic properties, wherein the first coating is coupled to the substrate; and

a second coating comprising a metal, a metal compound, a material having metallic properties or a compound having metallic properties, wherein the second coating is coupled to the first coating, and wherein the substrate, the first coating and the second coating form a surface that is resistant to deformation and wear.

Claim 29. A method for making a jewelry ring comprising a substrate, a first coating of a metal, a material having metallic properties, a metal compound, a metallic compound, a metal alloy and a metal carbide, and an external metal or metallic coating, the method comprising:

cutting, pressing, molding, casting, striking, extruding, sintering and/or shaping the substrate into a ring shape;

depositing the first coating onto the substrate; and

depositing the external metal or metallic coating onto the first coating, wherein the substrate, the first coating and the external metal or metallic coating form a surface that is resistant to deformation and wear.

Claim 30. The method of claim 29, wherein a surface is formed that substantially retains the color of the external metal or metallic coating.

Claim 31. The method of claim 1, further comprising subjecting the coated jewelry article or the coated component of the jewelry article to one or more additional layering processes to obtain a multi-coated jewelry article or multi-coated component of the jewelry article comprising a multi-coating, wherein the jewelry article or the component of the jewelry article, the first coating, the second coating and the one or more additional coatings form a surface that is resistant to deformation and wear.

Claim 32. The method of claim 31, wherein the jewelry article or coated component of the jewelry article exhibits a non-gray color or luster.

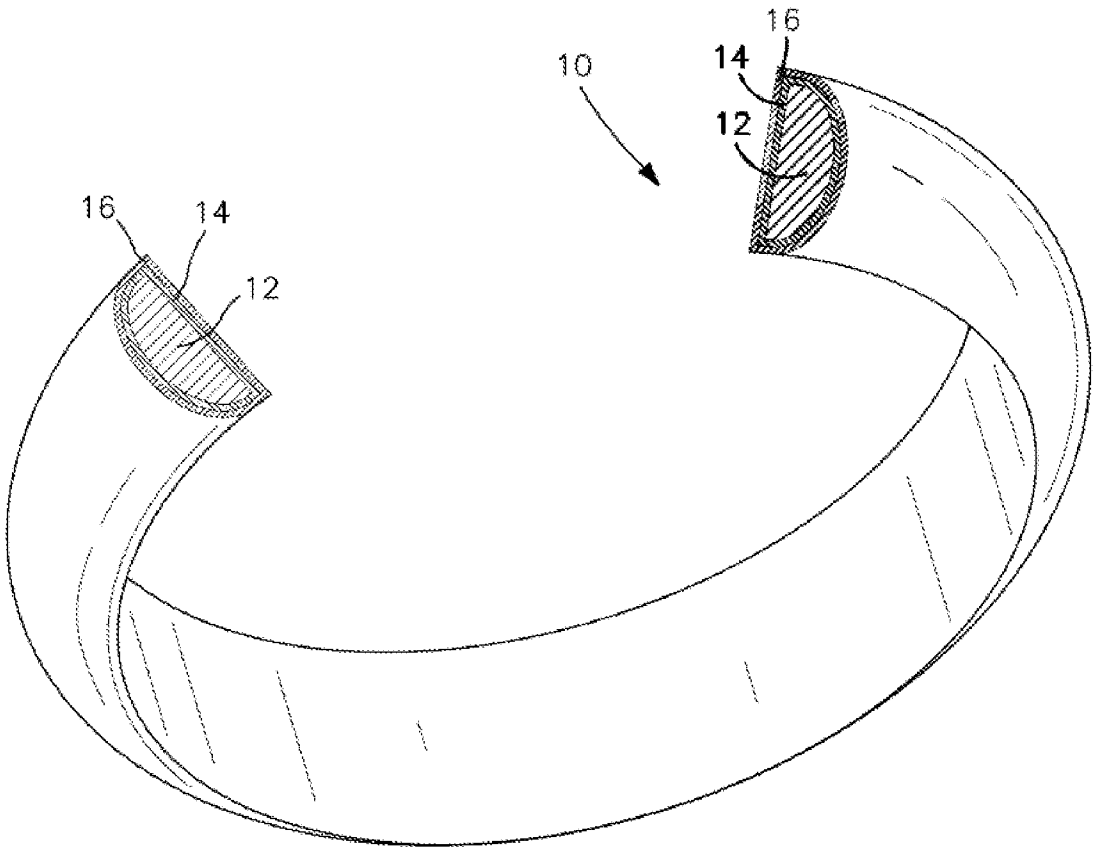

FIG. 1

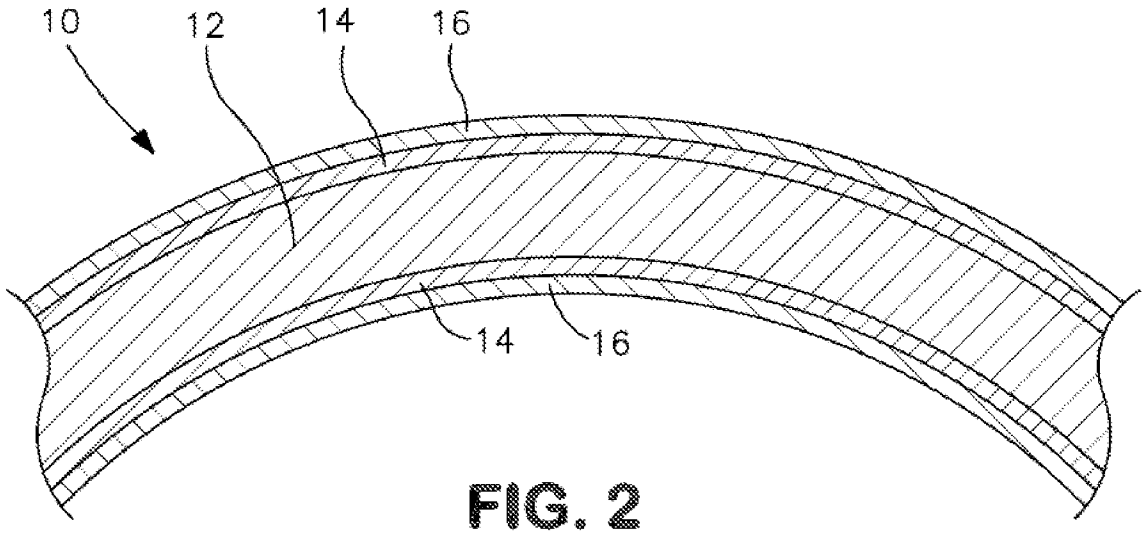

FIG. 2

			Cr/Steel 30/70	Cr/Steel 60/40	Cr/Steel 70/30	Cr/Steel 75/25	Cr/Steel 80/20	Cr/Steel 90/10
Carbon	C	0.03%	0.021%	0.012%	0.009%	0.008%	0.006%	0.003%
Manganese	Mn	2.00%	1.400%	0.800%	0.600%	0.500%	0.400%	0.200%
Silicon	Si	1.00%	0.700%	0.400%	0.300%	0.250%	0.200%	0.100%
Phosphorus	P	0.05%	0.032%	0.018%	0.014%	0.011%	0.009%	0.005%
Sulphur	S	0.03%	0.021%	0.012%	0.009%	0.008%	0.006%	0.003%
Chromium	Cr	17.00%	11.900%	6.800%	5.100%	4.250%	3.400%	1.700%
Molybdenum	Mo	2.50%	1.750%	1.000%	0.750%	0.625%	0.500%	0.250%
Nickel	Ni	12.00%	8.400%	4.800%	3.600%	3.000%	2.400%	1.200%
Iron	Fe	65.00%	45.500%	26.000%	19.500%	16.250%	13.000%	6.500%
		316 Steel%	70%	40%	30%	25%	20%	10%
		Pure Chrome %	30%	60%	70%	75%	80%	90%
		Total	100%	100%	100%	100%	100%	100%

FIG. 3

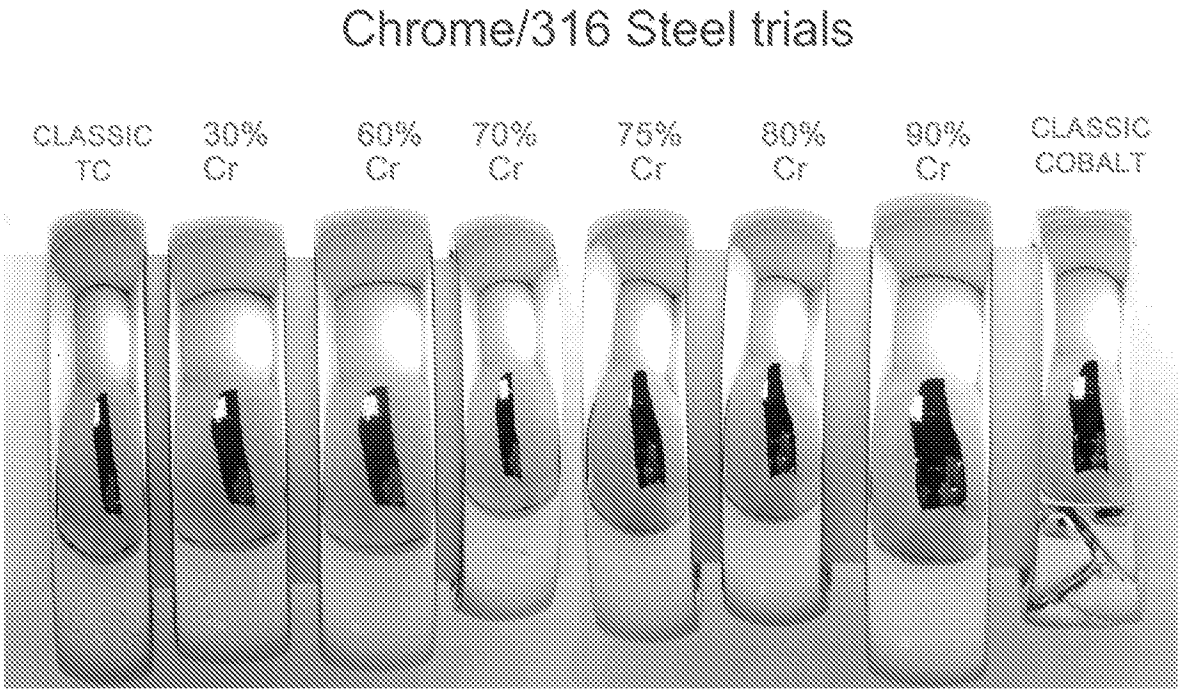
Chrome/316 Steel trials
CLASSIC TC
30% Cr
60% Cr
70% Cr
75% Cr
80% Cr
90% Cr
CLASSIC COBALT

FIG. 4

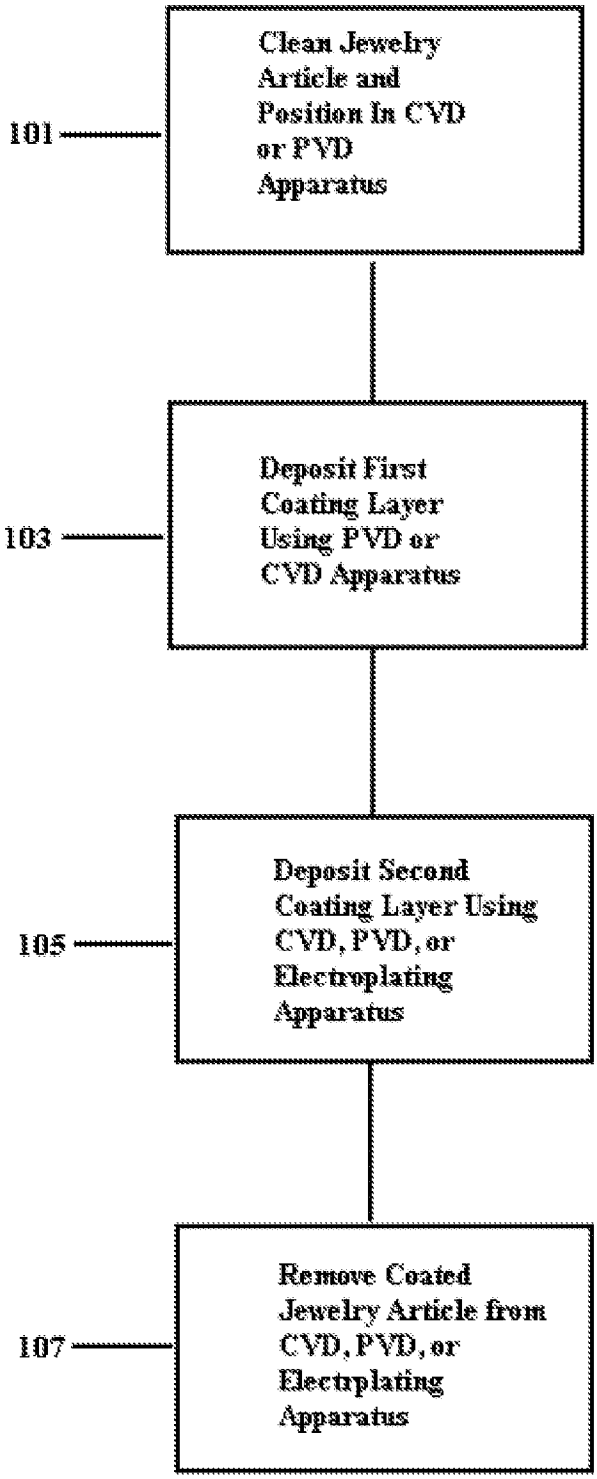
Clean Jewelry Article and Position In CVD or PVD Apparatus
101
Deposit First Coating Layer Using PVD or CVD Apparatus
103
Deposit Second Coating Layer Using CVD, PVD, or Electroplating Apparatus
105
Remove Coated Jewelry Article from CVD, PVD, or Electrplating Apparatus
107

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/040356

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A44C 27/00 (2012.01)
USPC - 63/34
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - A44C 9/00, 27/00; B05D 1/36; C23C 16/06 (2012.01)
USPC - 63/15, 34; 427/248.1, 250, 404

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,745,035 A (SAURER et al) 17 May 1988 (17.05.1988) entire document	1-7, 10-11, 17-22, 25-28, 31
---		---
Y		8-9, 13-16, 23-24, 29-30, 32
Y	US 2005/0208325 A1 (KAWAKAMI et al) 22 September 2005 (22.09.2005) entire document	8-9, 13-16, 23-24, 29-30, 32

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 August 2012	27 AUG 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/040356

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 12
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.