

PRECIOUS METAL ARTICLE WITH PLATING LAYER ON SURFACE AND PREPARATION METHOD THEREOF

FIELD

[0001] The present disclosure relates to the technical field of plating layer on the gold surface, in particular to a precious metal article with a plating layer on the surface and a preparation method thereof.

BACKGROUND

[0002] The gold products have the characteristics of bright color and desirable stability, are usually used as the ornaments and jewelry and are popular among wide spread consumers. The current production process of the gold product mainly comprises casting a wax mold, inverting a mold, surface trimming and shape-correction treatment. In order to improve glossiness of a surface of the gold product, the surface of the gold product is generally treated with an electroplating method.

[0003] CN106521594A discloses a processing method and device for processing K gold into gold natural color, the processing method comprises the following steps: manufacturing semi-finished jewelry products in advance; subjecting the semi-finished jewelry products to electroplating processing, so as to convert the external color of the semi-finished jewelry products to the gold natural color; and carrying out

surface treatment on the electroplated semi-finished jewelry products to form the finished jewelry products.

[0004] However, when the electroplating method is adopted to plate a film on the surface of the gold product, the film layer on the surface of the gold product is unstable and is prone to peel off.

[0005] CN107675136A discloses a method for Physical Vapor Deposition (PVD) film coating on surfaces of workpieces, the method comprises the following steps: putting workpieces to be plated in a film plating chamber, vacuumizing and heating the film plating chamber; then introducing argon gas, performing ion bombardment treatment on the workpieces to be plated; then introducing a working gas, applying a bias voltage to the workpieces to be plated, and depositing the plating layers with corresponding materials on the surfaces of the workpieces to be plated.

[0006] CN105803412A discloses a PVD coating on surface of airspeed head and a preparation method of PVD coating, wherein the method comprises a step of depositing a single metal plating layer on the polished surface of the airspeed head by using the physical vapor deposition method.

[0007] The aforementioned methods adopt a PVD method to plate a film on the surface of the workpiece, thereby improving the bonding force between the plating film and the workpiece to be plated. However, PVD

is only suitable for plating a film on the surface of a material with a high hardness at present, when the plating film is attached to a surface of the material with a low hardness (e.g., Mohs hardness of 2-3), the bonding force between the film layer and the substrate is still weak.

SUMMARY

[0008] The present disclosure serves to solve the problem in the prior art in regard to unstable plating layer on the gold surface, and provides a precious metal article having a plating layer on the surface and a preparation method thereof. The surface of the precious metal article in the present disclosure is formed with different kinds of film layers, the formed film layers have a stable structure, and may exhibit diverse colors.

[0009] In order to achieve the above objects, a first aspect of the present disclosure provides a precious metal article comprising a precious metal substrate and a physical vapor deposition layer attached to a surface of the precious metal substrate, wherein the precious metal is gold or silver.

[0010] In a second aspect, the present disclosure provides a method of preparing a precious metal article, the method comprises the following step: attaching the physical vapor deposition layer to a surface of the precious metal substrate by physical vapor deposition.

[0011] The film is plated on a surface of the precious metal substrate by adopting a physical vapor deposition method, so that a film layer with

rich and brilliant colors can be formed, the single color of the precious metal substrate may be diversified, and the color change of the precious metal substrate does not influence purity of the precious metal substrate. According to the preferred embodiment of the present disclosure, the precious metal substrate has a surface roughness within a range of 0.001-50 μ m, the precious metal substrate obtained after a cleaning process is subjected to baking under the temperature of 100-150 °C, the plating film can be easily formed on the surface of the precious metal substrate by means of physical vapor deposition, and the formed film layer has improved stability and abrasion resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 illustrates a schematic view of the structure of the precious metal article of Example 1;

[0013] FIG. 2 illustrates a schematic view of the structure of the precious metal article of Example 13;

[0014] FIG. 3 illustrates a schematic view of the structure of the precious metal article of Example 12.

[0015] Description of the reference numerals

[0016] 1. Precious metal substrate

[0017] 2. Physical vapor deposition layer

[0018] 3. Galvanic plating layer

[0019] 4. Transparent film layer

DETAILED DESCRIPTION

[0020] The terminals and any value of the ranges disclosed herein are not limited to the precise ranges or values, such ranges or values shall be comprehended as comprising the values adjacent to the ranges or values. As for numerical ranges, the endpoint values of the various ranges, the endpoint values and the individual point values of the various ranges, and the individual point values may be combined with one another to produce one or more new numerical ranges, which should be deemed have been specifically disclosed herein.

[0021] A first aspect of the present disclosure provides a precious metal article comprising a precious metal substrate 1 and a physical vapor deposition layer 2 attached to a surface of the precious metal substrate 1, wherein the precious metal is gold or silver.

[0022] Preferably, wherein the precious metal substrate 1 has a gold content of 33-99.99 wt%, more preferably 75-99.99 wt% (or 99-99.99 wt%), or the precious metal substrate 1 preferably has a silver content of 92.5-99 wt%.

[0023] If the precious metal substrate 1 is consisting of gold, which may be K gold or pure gold. The term “K gold” means a precious metal substrate 1 formed by melting gold in combination with silver, zinc,

copper, palladium or nickel, and the term “pure gold” means that the content of gold in the precious metal substrate 1 is not less than 99wt%. If the precious metal substrate 1 is composed of silver, which may be pure silver having a purity of 99.9%, pure silver, or pure silver having a purity of 92.5%.

[0024] The physical vapor deposition layer 2 is attached to the surface of the precious metal substrate 1 by adopting a physical vapor deposition mode, and the film layer formed by attaching the physical vapor deposition layer 2 to the precious metal substrate 1 is stable, wear-resistant and its color will not easily fade.

[0025] Preferably, the thickness of the physical vapor deposition layer 2 is within a range of 10nm-50 μ m, more preferably 0.04 μ m-2 μ m.

[0026] When the physical vapor deposition layer has a thickness within the thickness range, the bonding between the physical vapor deposition layer 2 and the precious metal substrate 1 is more firm; in addition, the physical vapor deposition layer 2 does not influence purity of precious metal substrate 1 per se during a process of detecting the precious metal article.

[0027] According to the present disclosure, the physical vapor deposition layer 2 may be a single plating layer or a multi-layer plating layer. For example, a single layer of the same kind may be integrally deposited on the surface of the precious metal substrate 1 by physical vapor deposition,

specifically, the material of the physical vapor deposition layer 2 may be a commonly used metal, alloy, metal oxide, metal nitride, metal carbide, metal fluoride, metal sulfide, metal boride or diamond-like carbon (DLC) plating film having a color, such as Ni, Ti, Zn, Cr, Mg, Nb, Sn, Al, In, Fe, Zr, Si, Cu, Ta, Ge, Ag, Co, Au, Gd, La, Y, Ce, W, Hf, Mo, CrN, TiN, TiAlCN, TiCN, TiAlN, AlTiN, TiB₂, ZrN, FeCo, AlSi, TiSi, CrSi, ZnAl, TiZn, TiAl, TiZr, TiSi, TiNi, NiAl, NiV, NiFe, gold-copper alloy or DLC, preferably gold-copper alloy.

[0028] Provided that the plating layer on the surface of the precious metal substrate 1 is CrN, the precious metal article exhibits a gray black color; if the plating layer on the surface of the precious metal substrate 1 is TiN, the precious metal article has a champagne gold color; if the plating layer on the surface of the precious metal substrate 1 is TiAlN, the precious metal article exhibits a coffee color; if the plating layer on the surface of the precious metal substrate 1 is DLC, the precious metal article has a black color.

[0029] In addition, the present disclosure may use a physical vapor deposition method to deposit a multi-layer plating layer on the surface of the precious metal substrate 1, and finally form a polychrome color. For instance, the areas which do not need to be dyed can be shielded by a sheltering method, the surface of the precious metal substrate 1 is then attached with a physical vapor deposition layer 2, such that the surface of

the finally prepared precious metal article presents distinct patterns.

[0030] A plurality of coatings can also be formed on the surface of the precious metal substrate 1 in advance, and then a part of the color deposited on the precious metal substrate 1 may be removed by a the computer numerical control (CNC) machine tool or a manual grinding and polishing method, such that patterns with different colors can be formed on the surface of the finally produced precious metal article.

[0031] According to the present disclosure, the precious metal substrate 1 may have a surface roughness of $0.001\mu\text{m}$ - $50\mu\text{m}$, preferably $0.005\mu\text{m}$ - $0.2\mu\text{m}$.

[0032] The surface roughness is denoted as Ra, which means the unevenness of the small spacing, tiny peak and valley of the processed surface, and can be directly tested with a surface roughness measuring instrument. If the precious metal substrate 1 itself satisfies the surface roughness within a range of $0.001\mu\text{m}$ - $50\mu\text{m}$, the subsequent steps may be directly performed. If the precious metal substrate 1 is made of a material that does not satisfy the surface roughness within a range of $0.001\mu\text{m}$ - $50\mu\text{m}$, the precious metal substrate 1 may be treated through a chemical or mechanical method, which is not particularly limited in the present disclosure, as long as the above roughness can be satisfied.

[0033] The surface roughness of the precious metal substrate 1 satisfies the above conditions, it is easier to perform film plating on the surface of

the precious metal substrate. If the surface roughness is too low, the bonding firmness of the film layer and the precious metal substrate is reduced; if the surface roughness is too large, the color and luster of the finally produced precious metal article are affected.

[0034] In the present disclosure, the glossiness of the gold article 1 may be 700-900 Gu. In the present disclosure, Gu means an English term “gloss unit”, and 1 gloss unit =1 Gu. When measuring the glossiness, the specular glossiness of the precious metal article is measured by a glossiness measuring instrument under a geometrical condition of an angle 60 °.

[0035] According to the present disclosure, the gold content of the physical vapor deposition layer 2 may be below 0.1 wt% or above 33 wt%, preferably the gold content of the physical vapor deposition layer 2 is below 0.01 wt% or within a range of 70-90 wt%, more preferably the gold content of the physical vapor deposition layer 2 is within a range of 0.001-0.008 wt% or 75-85 wt%.

[0036] In a second aspect, the present disclosure provides a method of preparing a precious metal article, the method comprises the following step: attaching the physical vapor deposition layer 2 to a surface of the precious metal substrate 1 by physical vapor deposition.

[0037] According to the present disclosure, the conditions of physical vapor deposition cause that the physical vapor deposition layer 2 has a

thickness within a range of 10nm-50 μ m (such as 10nm, 20nm, 30nm, 50nm, 80nm, 0.1 μ m, 0.15 μ m, 0.2 μ m, 0.25 μ m, 0.3 μ m, 0.5 μ m, 0.8 μ m, 1 μ m, 2 μ m, 10 μ m, 30 μ m, 50 μ m, or any value in between the aforementioned numerical values), preferably within a range of 0.04 μ m-2 μ m.

[0038] The present disclosure does not impose a specific requirement on the physical vapor deposition method, which may be vacuum evaporation plating, vacuum sputtering coating, or vacuum ion plating, and preferably vacuum ion plating.

[0039] If the vacuum evaporation plating process is adopted, a vacuum evaporation system is utilized, both the precious metal substrate 1 and the metal to be plated are placed in the vacuum evaporation system, the precious metal substrate 1 is heated under the condition that the vacuum degree is $5-7 \times 10^{-3}$ Pa, and the material to be plated is arranged in an evaporation vessel. The material to be plated can be a metal material (such as aluminum) for color development, the evaporation voltage is adjusted to heat the evaporation vessel to the evaporation temperature (e.g., 800-1,500 $^{\circ}$ C) of the material to be plated, so as to perform the film plating on the surface of the precious metal substrate 1, then the annealing is carried out under the protection of an inert gas (such as argon gas).

[0040] If the vacuum sputtering coating is adopted, the precious metal

substrate 1 is heated to 100-250 °C under the condition that the vacuum degree is within a range of $1 \times 10^{-2} \text{Pa}$ - $7 \times 10^{-3} \text{Pa}$, and the surface oxidation film is removed from the metal target to be plated. Under the condition of plasma, the positive ions formed after ionization of argon gas will bombard surface of the target material, the magnetron sputtering is used for plating a film on the surface of the precious metal substrate 1, the sputtering voltage is selected to be 300-700V, and the metal to be plated forms a film on the surface of the precious metal substrate 1.

[0041] In the present disclosure, the vacuum ion plating comprises the following steps: placing the precious metal substrate 1 under a vacuum condition, then heating the precious metal substrate 1, starting a metal target, injecting a gas, loading a bias voltage, and performing film plating on the surface of the precious metal substrate 1.

[0042] Wherein, the vacuum degree is within a range of $1 \times 10^{-2} \text{Pa}$ - $7 \times 10^{-3} \text{Pa}$ when the precious metal substrate 1 is placed under the vacuum condition.

[0043] After gas injection, the vacuum degree is within a range of $1 \times 10^{-2} \text{Pa}$ - $9.5 \times 10^{-1} \text{Pa}$.

[0044] The temperature will influence the bonding force between the plating layer and the precious metal substrate and the color of the plating layer, particularly when the rose gold plating layer is produced, the heating temperature in the furnace is generally within a range of

100-250 °C, and preferably 200 °C.

[0045] The time of plating film is within a range of 2-2,000min, in the present disclosure, the deposition time is associated with plating layer to be plated according to the different target materials, the target materials are divided into an arc target, a column target and a flat target, the ion particles of the arc target are the coarsest, followed by the ion particles of the flat target, the ion particles of the column target are the finest, as a result, the arc target can be quickly colored, followed by the flat target, the column target is slowly colored, taking rose gold color as an example, the plating time of the arc target is about 10min, the plating time of the column target is 20-30min; in addition, the time of plating the magic color film is about 10min, the time of plating a purple film is the shortest, such as 2-3min, thus the purple plating layer has a large color difference and a unstable color.

[0046] The material of the metal target is one or more selected from the group consisting of nickel, zinc, magnesium, tin, iron, chromium, silicon, copper, titanium, zirconium, molybdenum, tungsten, aluminum, niobium, indium, tantalum, germanium, silver, gold, cobalt, gadolinium, lanthanum, yttrium, cerium, hafnium, tungsten, gold-copper alloy, stainless steel, and alloy or oxide, nitride, carbide, fluoride, sulfide and boride thereof, preferably gold-copper alloy. In the gold-copper alloy, the atomic ratio of gold to copper is (75-85): (15-25), preferably 85:15 or 75: 25.

[0047] The gas comprises a protective gas and a toning gas, the protective gas is an inert gas, and the toning gas is one or more selected from the group consisting of nitrogen gas, acetylene, methane and oxygen gas; wherein the argon gas is used as protective gas for adjusting the vacuum degree, and the gas flow of the protective gas may be within a range of 20-200sccm, preferably 20-150sccm; the nitrogen gas, acetylene, methane or oxygen gas are used as the working gas, which may combine with the metal to form a plating film, and is used for adjusting color of the plating layer, the gas flow rate of the working gas is within a range of 50-500sccm.

[0048] Wherein the applied bias voltage is 10-150V, and the duty ratio is 10-80%; in the present disclosure, the term “duty ratio” refers to the ratio of the time occupied by pulses relative to the total time during a period of continuous operation. In the present disclosure, the higher is the bias voltage, the larger is the brightness; however, if the bias voltage exceeds a certain value, the edge of the precious metal article will turn yellow; thus the effect is optimal when the applied bias voltage is defined in the above range.

[0049] The target material current of the metal target is as follows: the current of column target is within a range of 3-120A, preferably 20-120A, the current of arc target is within a range of 50-200A. In the present disclosure, the larger is the current, the coarser are the ion particles,

which results in the hazy plating layer on the surface of the precious metal article, that is, the glossiness is undesirable, especially the current of arc target has the largest influence on the glossiness, the current of the column target has a slightly small influence on the glossiness, the suitable current is vital for the glossiness of the plating layer. Therefore, when the current of the target material is limited to the above range, it produces the best effect.

[0050] The deposition time is related to a shape of the target material, and the film layer to be plated, the specific details will be formulated in the Examples.

[0051] The metal target and the protective gas can be selected according to the color displayed by the finally produced precious metal article, wherein the metal may be a single metal, for example, the selected metal target is a titanium target, the protective gas is argon gas, the working gas is nitrogen gas, the gas flow rate is 100-350sccm, the finally produced precious metal article exhibits a golden yellow color. The metal can also be a mixture of multiple metals, for example, the selected metal target is a titanium aluminum target, the protective gas is argon gas, the working gas is nitrogen gas, the gas flow rate is 100-350sccm, and the finally produced precious metal article exhibits a brown color. The specific content will be elaborated in the Examples.

[0052] According to the present disclosure, the glow cleaning can be

implemented prior to the physical vapor deposition, and the glow cleaning conditions comprise: the gas flow rate of the protective gas is within a range of 100-320sccm, preferably 280-320sccm, the applied bias voltage is within a range of 380-1,000V, preferably 380-420V, and the duty ratio is 10-80%, preferably 48-52%; the time is 160-720s, preferably 160-200s.

[0053] In the present disclosure, the method may further comprise a step of subjecting a surface of the precious metal substrate 1 to a surface treatment, such that the precious metal substrate 1 has a surface roughness within a range of 0.001 μ m-50 μ m.

[0054] The surface treatment method of the precious metal substrate 1 is not particularly limited herein, and a physical polishing or a chemical etching method may be employed, as long as the condition that the surface roughness of the precious metal substrate 1 is within a range of 0.001 μ m-50 μ m can be achieved. The precious metal substrate 1 has a surface roughness within a range of 0.001 μ m-50 μ m (e.g., 0.02 μ m, 0.05 μ m, 0.2 μ m, 0.3 μ m, 1 μ m, or any value therebetween), preferably 0.005 μ m-0.2 μ m.

[0055] Preferably, the method further comprises rinsing the surface-treated precious metal substrate 1 by means of the following modes: ultrasonically washing the precious metal substrate 1 for 1-15min under the ultrasonic frequency condition of 20-30kHz, and/or cleaning a

surface of the precious metal substrate 1 with 95-98 wt% of alcohol.

[0056] In the present disclosure, different cleaning methods can be selected depending on the surface structure, area and cleanliness degree of the precious metal substrate 1. Generally, there are two kinds of cleaning methods.

[0057] The first method comprises the following steps: ultrasonically washing the precious metal substrate 1 for 1-15min under the condition of ultrasonic frequency 20-30kHz; it should be noted in the present disclosure that the ultrasonic cleaning time can be prolonged under the special conditions, after the ultrasonic cleaning is finished, the precious metal substrate shall be washed with clean water for more than 6 times to remove residues of the surface detergent; after the washing process is finished, the baking treatment needs to be carried out for dehydration and roasting.

[0058] The second method comprises the following steps: if the surface of the precious metal substrate 1 is clean, there is not an oxide layer, the ultrasonic cleaning is not required, a surface of the precious metal substrate 1 may be directly wiped with 95-98 wt% of alcohol.

[0059] In the present disclosure, the cleaning method may be the first method and/or the second method, and preferably, the cleaning method may be the first method and the second method.

[0060] The precious metal substrate 1 is subjected to ultrasonic treatment

and/or washing with alcohol under the above conditions, so that the bonding force between the physical vapor deposition layer 2 and the precious metal substrate 1 can be further improved. In addition, a film layer with the thickness of 10nm-50 μ m can be formed on the surface of the precious metal substrate within a short time, and the formed film layer is more stable.

[0061] Preferably, the method can further comprise a step of baking the ultrasonically treated precious metal substrate 1, the baking temperature is 100-150 $^{\circ}$ C, and the baking time is 5-30min.

[0062] The method for baking the precious metal substrate is not particularly limited in the present disclosure, as long as it can be ensured that the temperature is maintained between 100-150 $^{\circ}$ C, and for example, an oven may be utilized.

[0063] Moreover, in order to improve the abrasion resistance and brightness of the physical vapor deposition layer 2, a galvanic plating layer 3 and/or a transparent film layer 4 may be formed on the surface of the physical vapor deposition layer, that is, the precious metal article of the present disclosure comprises: a precious metal substrate 1, and a physical vapor deposition layer 2 and a galvanic plating layer 3 (as shown in FIG. 2) which are sequentially attached to the surface of the precious metal substrate 1; or a precious metal article of the present disclosure comprises: a precious metal substrate 1, and a physical vapor deposition

layer 2, a galvanic plating layer 3 and a transparent film layer 4 (as shown in FIG. 3) which are sequentially attached to the surface of the precious metal substrate 1; or a precious metal article of the present disclosure comprises: a precious metal substrate 1, and a physical vapor deposition layer 2 and a transparent film layer 4 which are sequentially attached to the surface of the precious metal substrate 1.

[0064] The galvanic plating layer 3 has a thickness within a range of 0.05-50 μ m, preferably 0.1-1.5 μ m, and in the present disclosure, if the thickness of the galvanic plating layer 3 is limited to the above range, the glossiness of the film layer can be increased. The material of the galvanic plating layer 3 may be gold-copper alloy, wherein the weight ratio of the contents of gold and copper in the gold-copper alloy is (75-85): (15-25), preferably 85:15 or 75: 25. The galvanic plating solution in the galvanic plating process is not particularly limited, it may be a conventional choice in the technical field, such as 3G brand gold plating solution, wherein the gold trichloride content is 20-25g/L, the potassium pyrophosphate content is 40-50g/L, the citrate content is 60-80g/L, the additive content is 0.2-0.5g/L, and the gold content is 24K. The galvanic plating current is within a range of 0.5-0.9A, preferably 0.7-0.8A; the temperature is within a range of 50-80 $^{\circ}$ C, preferably 65-75 $^{\circ}$ C; the galvanic plating time is 1-5min, preferably 2-3 min. In the present disclosure, the galvanic plating conditions are limited to the above ranges, the thickness of the galvanic

plating layer 3 defined in the present disclosure can be formed to have a thickness.

[0065] The thickness of the transparent film layer 4 is within a range of 0.0001-10 μ m, preferably 0.0005-0.1 μ m, and the material of the transparent film layer 4 may be a fluoride; for example, the fluoride may be an AF pill; in the present disclosure, the AF pill is commercially available, for example, from Huizhou Momet electronic Technology Co., Ltd., with a model number TS-2AB.

[0066] The transparent film layer is prepared by adopting a vacuum evaporation plating mode, wherein the evaporation is performed for 170-190s under the condition that the current of the evaporation source is 700-750A; the evaporation is then performed for 170-190s under the condition that the current of the evaporation source is 750-800A; the evaporation is subsequently performed for 410-430s under the condition that the current of the evaporation source is 800-900A.

[0067] In addition, the vacuum evaporation plating is carried out under the conditions consisting of a normal temperature, a vacuum degree within a range of 3×10^{-7} Pa- 6×10^{-7} Pa, an argon gas flow of 50-60sccm, an oxygen gas flow of 70-80sccm, an applied bias voltage of 30-40V, the duty ratio of 30-40%, the time is 20-30 min; the target material is an aluminum target and a silicon target; when the aluminum target is selected, the current is 2-3A, and when the silicon target is selected, the

current is 2-3A.

[0068] In the present disclosure, the thickness and material of the transparent film layer 4 are within the above-defined range, such that the formed film layer is more stable, the abrasion resistance is stronger, and the formed color is more durable and does not fade.

[0069] The present disclosure will be described in detail below with reference to examples.

[0070] The detection methods involved in the following examples are as follows:

[0071] Glossiness: the glossiness of the precious metal articles was measured with a LS192 glossiness instrument at an angle of 60°.

[0072] Abrasion resistance: the WS-97 coating adhesive force scratch tester developed by the ZhongkeKaihua Technology Development Co., Ltd. was adopted to carry out scratch test on the precious metal article. The scratch test used a scribe with a smooth conical tip to carve the surface of the coating under the gradually increasing load until the coating was damaged, and the load applied when the coating was damaged was a critical load, which was taken as the measurement of the adhesive strength of the plating layer and the base. The loading rate was set to 10N/min, the applied load was set to 30N, the scratch speed was set to 2mm/min, and the scratch length was 5 mm.

[0073] Example 1

[0074] The example aimed to prepare a pure gold article with a coffee TiAlN-plated film with the method of the present disclosure, and its structure was shown in FIG. 1.

[0075] (1) Pretreatment

[0076] Selection of a precious metal substrate 1: the pure gold was selected as the material of a precious metal substrate 1, which had a surface roughness of 0.02 μ m;

[0077] Cleaning: ultrasonically cleaning the pure gold for 10min by using distilled water under the ultrasonic frequency condition of 20kHz, the pure gold subjected to ultrasonic cleaning was baked at 150 $^{\circ}$ C for 30min; then the surface was wiped and cleaned with a dust-free fabric dipped in 98 wt% alcohol;

[0078] Vacuumization of the furnace: the baked pure gold was placed into a vacuum furnace, and the vacuum degree was adjusted to 3×10^{-3} Pa in order to ensure the clean vacuum environment in the furnace.

[0079] (2) Depositing a physical vapor deposition layer 2

[0080] Glow cleaning: the glow cleaning was performed under the conditions consisting of an argon gas flow rate of 300sccm, an applied bias voltage of 400V, a duty ratio of 50% and a time of 400s.

[0081] The temperature in the furnace was adjusted to 200 $^{\circ}$ C, the TiAl column target was activated, wherein the Ti/Al atomic ratio was 7: 3, the current of the target material was 25A; the protective gas argon gas was

injected with a gas flow of 130sccm, and nitrogen gas was injected with a gas flow of 150sccm, the vacuum degree was adjusted to 3.0×10^{-1} Pa, the applied bias voltage was 100V and the duty ratio was 50%, the depositing process was performed for 30min, thereby forming a coffee TiAlN film with a thickness of 0.3 μ m on the surface of the pure gold.

[0082] Example 2

[0083] The example aimed to prepare a pure gold article with a gray-black CrN-plated film with the method of the present disclosure.

[0084] (1) Pretreatment

[0085] Selection of a precious metal substrate 1: the pure gold was selected as the material of a precious metal substrate 1, which had a surface roughness of 0.05 μ m;

[0086] Cleaning: ultrasonically cleaning the pure gold for 5min by using distilled water under the ultrasonic frequency condition of 30kHz, the pure gold subjected to ultrasonic cleaning was baked at 150 $^{\circ}$ C for 30min; then the surface was wiped and cleaned with the 98 wt% alcohol;

[0087] Vacuumization of the furnace: the baked pure gold was placed into a vacuum furnace, and the vacuum degree was adjusted to 3×10^{-3} Pa, and the temperature in the furnace was adjusted to 200 $^{\circ}$ C.

[0088] (2) Depositing a physical vapor deposition layer 2

[0089] Glow cleaning: the glow cleaning was performed under the conditions consisting of an argon gas flow rate of 300sccm, an applied

bias voltage of 400V, a duty ratio of 50% and a time of 400s.

[0090] A high-purity medium-frequency chromium arc target was activated, wherein the current of the target material was 100A; nitrogen gas was injected with a gas flow of 230sccm, the vacuum degree was adjusted to 3.0×10^{-1} Pa, the applied bias voltage was 100V and the duty ratio was 50%, the depositing process was performed for 5min, thereby forming a gray black CrN film with a thickness of 0.15 μ m on the surface of the pure gold.

[0091] Example 3

[0092] The example aimed to prepare a pure gold article with a black DLC-plated film with the method of the present disclosure.

[0093] (1) Pretreatment

[0094] Selection of a precious metal substrate 1: the pure gold was selected as the material of a precious metal substrate 1, which had a surface roughness of 0.2 μ m;

[0095] Cleaning: ultrasonically cleaning the pure gold for 10min by using distilled water under the ultrasonic frequency condition of 25kHz, the pure gold subjected to ultrasonic cleaning was baked at 150 $^{\circ}$ C for 30min; then the surface was wiped and cleaned with the 95wt% alcohol;

[0096] Vacuumization of the furnace: the baked pure gold was placed into a vacuum furnace, and the vacuum degree was adjusted to 3×10^{-3} Pa.

[0097] (2) Depositing a physical vapor deposition layer 2

[0098] Glow cleaning: the glow cleaning was performed under the conditions consisting of an argon gas flow rate of 300sccm, an applied bias voltage of 400V, a duty ratio of 50% and a time of 400s.

[0099] The temperature in the furnace was adjusted to 200 °C, the chromium target column target was activated, the current of the target material was 20A; the protective gas argon gas was injected with a gas flow of 130sccm, the acetylene gas was injected with a gas flow of 200sccm, the applied bias voltage was 50V and the duty ratio was 50%, the depositing process was performed for 50min, thereby forming a black film layer with a thickness of 0.5μm on the surface of the pure gold. Then the power supply of the chromium target column target was shut off, the acetylene gas was injected with a gas flow of 200sccm, the applied bias voltage was 1,000V, the duty ratio was 80%, the depositing process was performed for 5h, such that a DLC film with the thickness of 0.1μm was formed on the surface of the pure gold.

[00100] Example 4

[00101] The example aimed to prepare a pure gold article with a golden yellow color TiN-plated film with the method of the present disclosure.

[00102] (1) Pretreatment

[00103] Selection of a precious metal substrate 1: the pure gold was selected as the material of a precious metal substrate 1, which had a

surface roughness of 0.03 μm ;

[00104] Cleaning: ultrasonically cleaning the pure gold for 10min by using distilled water under the ultrasonic frequency condition of 25kHz, the pure gold subjected to ultrasonic cleaning was baked at 150 $^{\circ}\text{C}$ for 30min; then the surface was wiped and cleaned with the 98 wt% alcohol;

[00105] Vacuumization of the furnace: the baked pure gold was placed into a vacuum furnace, and the vacuum degree was adjusted to $3\times 10^{-3}\text{Pa}$ in order to ensure the clean vacuum environment in the furnace.

[00106] (2) Depositing a physical vapor deposition layer 2

[00107] Glow cleaning: the glow cleaning was performed under the conditions consisting of an argon gas flow rate of 300sccm, an applied bias voltage of 400V, a duty ratio of 50% and a time of 400s.

[00108] The Ti column target was activated, the current of the target material was 20A. The protective gas argon gas was injected with a gas flow of 130sccm, and nitrogen gas was injected with a gas flow of 200sccm, the vacuum degree was adjusted to $5\times 10^{-1}\text{Pa}$. The applied bias voltage was 100V, the duty ratio was 50%, the depositing process was performed for 30min, thereby forming a golden yellow TiN film with a thickness of 0.2 μm on the surface of the pure gold.

[00109] Example 5

[00110] The example aimed to prepare a 18K gold article with a coffee TiAlN-plated film with the method of the present disclosure.

[00111] The plating layer was performed on a surface of the pure gold according to the same method as that in Example 1, except that the pure gold was replaced by the 18K gold.

[00112] Example 6

[00113] The example aimed to prepare a pure gold article with a rose gold and partial reddish color using the method of the present disclosure.

[00114] (1) Pretreatment

[00115] Selection of a precious metal substrate 1: the pure gold was selected as the material of a precious metal substrate 1, which had a surface roughness of 0.02 μ m;

[00116] Cleaning: ultrasonically cleaning the pure gold for 10min by using distilled water under the ultrasonic frequency condition of 20kHz, the pure gold subjected to ultrasonic cleaning was baked at 150 $^{\circ}$ C for 30min; then the surface was wiped and cleaned with a dust-free fabric dipped in 98 wt% alcohol;

[00117] Vacuumization of the furnace: the baked pure gold was placed into a vacuum furnace, and the vacuum degree was adjusted to 3×10^{-3} Pa in order to ensure the clean vacuum environment in the furnace.

[00118] (2) Depositing a physical vapor deposition layer 2

[00119] Glow cleaning: the glow cleaning was performed under the conditions consisting of an argon gas flow rate of 300sccm, an applied

bias voltage of 400V, a duty ratio of 50% and a time of 400s.

[00120] The temperature in the furnace was adjusted to 200 °C, the gold-copper target column target was activated, wherein the Au/Cu atomic ratio was 75: 25, the current of the target material was 3A. The protective gas argon gas was injected with a gas flow of 130sccm, the vacuum degree was adjusted to 3×10^{-1} Pa. The applied bias voltage was 100V and the duty ratio was 50%, the depositing process was performed for 20min, thereby forming a rose gold and partial reddish color film layer with a thickness of 0.1 μ m on the surface of the pure gold.

[00121] Example 7

[00122] The example aimed to prepare a pure gold article with rose gold and partial purple color using the method of the present disclosure.

[00123] The plating layer was performed on the surface of the pure gold according to the same method as that in Example 6, except that the TiAl column target was activated, wherein the Ti/Al atomic ratio was 7: 3, the current of the target material was 20A; the protective gas argon gas was injected with a gas flow of 130sccm, and nitrogen gas was injected with a gas flow of 200sccm, the vacuum degree was adjusted to 5.0×10^{-1} Pa, the applied bias voltage was 100V and the duty ratio was 50%, the depositing process was performed for 30min, thereby forming a rose gold and partial purple color film layer with a thickness of 0.3 μ m on the surface of the pure gold.

[00124] Example 8

[00125] The example aimed to prepare a pure gold article with a purple color using the method of the present disclosure.

[00126] The plating layer was performed on the surface of the pure gold according to the same method as that in Example 6, except that the temperature in the furnace was adjusted to 200 °C, the Ti target arc target was activated, the current of the target material was 100A; the protective gas argon gas was injected with a gas flow of 130sccm, the vacuum degree was adjusted to 2.0×10^{-1} Pa; the oxygen gas was injected with a gas flow of 100sccm; the applied bias voltage was 100V, the duty ratio was 50%, the depositing process was performed for 3min, thereby forming a film with a thickness of 0.1 μ m on the surface of the pure gold.

[00127] Example 9

[00128] The example aimed to prepare a pure gold article with a violaceous color using the method of the present disclosure.

[00129] The plating layer was performed on the surface of the pure gold according to the same method as that in Example 6, except that the temperature in the furnace was adjusted to 260 °C, the TiAl target arc target was activated, the atomic ratio of Ti/Al was 7:3, the current of the target material was 90A; the nitrogen gas was injected with a gas flow of 240sccm, the vacuum degree was adjusted to 6.0×10^{-1} Pa; the applied bias voltage was 120V and the duty ratio was 40%, the depositing

process was performed for 20min, thereby forming a film with a thickness of 0.3 μ m on the surface of the pure gold.

[00130] Example 10

[00131] The example aimed to prepare a pure gold article with a champagne gold color using the method of the present disclosure.

[00132] The plating layer was performed on the surface of the pure gold according to the same method as that in Example 6, except that the temperature in the furnace was adjusted to 200 $^{\circ}$ C, the Ti target arc target was activated, the current of the target material was 80A; the protective gas argon gas was injected with a gas flow of 130sccm, the vacuum degree was adjusted to 3.0×10^{-1} Pa; the nitrogen gas was injected with a gas flow of 100sccm; the applied bias voltage was 80V, the duty ratio was 60%, the depositing process was performed for 5min, thereby forming a film with a thickness of 0.1 μ m on the surface of the pure gold.

[00133] Example 11

[00134] The example aimed to prepare a pure gold article with a magic color using the method of the present disclosure.

[00135] The plating layer was performed on the surface of the pure gold according to the same method as that in Example 6, except that the temperature in the furnace was adjusted to 150 $^{\circ}$ C, the Ti target arc target was activated, the current of the target material was 100A; the protective gas argon gas was injected with a gas flow of 130sccm, the vacuum

degree was adjusted to $3.0 \times 10^{-1} \text{Pa}$; the oxygen gas was injected with a gas flow of 100sccm; the applied bias voltage was 100V, the duty ratio was 50%, the depositing process was performed for 10min, thereby forming a film with a thickness of $0.2 \mu\text{m}$ on the surface of the pure gold.

[00136] Example 12

[00137] The example aimed to prepare a pure gold article with the method of the present disclosure, and its structure was illustrated in FIG. 3.

[00138] A gold article was prepared according to the same method as that in Example 1, except that a galvanic plating layer 3 and a transparent film layer 4 were further formed on the surface of the physical vapor deposition layer 2.

[00139] (1) Pretreatment

[00140] Selection of a precious metal substrate 1: the pure gold was selected as the material of a precious metal substrate 1, which had a surface roughness of $0.02 \mu\text{m}$;

[00141] Cleaning: ultrasonically cleaning the pure gold for 10min by using distilled water under the ultrasonic frequency condition of 25kHz, the surface was then wiped and cleaned with a dust-free fabric dipped in 98 wt% alcohol; the cleaned pure gold was subjected to baking at $150 \text{ }^{\circ}\text{C}$ for 30min;

[00142] Vacuumization of the furnace: the baked pure gold was placed

into a vacuum furnace, and the vacuum degree was adjusted to $3 \times 10^{-3} \text{Pa}$ in order to ensure the clean vacuum environment in the furnace.

[00143] (2) Depositing a physical vapor deposition layer 2

[00144] Glow cleaning: the glow cleaning was performed under the conditions consisting of an argon gas flow rate of 300sccm, an applied bias voltage of 400V, a duty ratio of 50% and a time of 400s.

[00145] The temperature in the furnace was adjusted to 200 °C, the gold-copper target column target was activated, wherein the Au/Cu atomic ratio was 75: 25, the current of the target material was 3A. The protective gas argon gas was injected with a gas flow of 130sccm, the vacuum degree was adjusted to $3 \times 10^{-1} \text{Pa}$. The applied bias voltage was 100V and the duty ratio was 50%, the depositing process was performed for 20min, thereby forming a rose gold and partial reddish color film layer with a thickness of 0.1 μm on the surface of the pure gold.

[00146] (3) Galvanic plating layer 3

[00147] A galvanic plating layer with a thickness of 0.2 μm was formed by adopting a galvanic plating process under the conditions consisting of a galvanic plating current of 0.8A, a temperature of 70 °C and the galvanic plating time of 2min;

[00148] (4) transparent film layer 4

[00149] The pure gold having a surface plated with the physical vapor deposition layer 2 and the galvanic plating layer 3 was placed in a

vacuum furnace, and subjected to film plating by adopting a vacuum evaporation plating mode. The vacuum degree was adjusted to 2.0×10^{-2} Pa, the argon gas was injected with a gas flow of 60sccm; the vacuum degree was adjusted to 1.5×10^0 Pa, the glow cleaning was performed for 180s, the oxygen gas was injected with a gas flow of 80sccm, the vacuum degree was adjusted to 4.0×10^{-1} Pa, the aluminum target and the silicon target were activated and operated for 90s and 180s respectively, the power sources of the aluminum target and the silicon target were then shut off; the power supply of the evaporation source was activated, the AF pill was subjected to evaporation for 180s under the condition that the current of the evaporation source was 720A; then subjected to evaporating for 180s under the condition that the current of the evaporation source was 780A; and subsequently subjected to evaporation for 420s under the condition that the current of the evaporation source was 850A, thereby forming a transparent film layer 4 having a thickness of $0.01 \mu\text{m}$.

[00150] Example 13

[00151] The example aimed to prepare a pure gold article with the method of the present disclosure, its structure was shown in FIG. 2.

[00152] The gold article was prepared according to the same method as that in Example 12, except that only a galvanic plating layer 3 was formed on the surface of the physical vapor deposition layer 2.

[00153] A galvanic plating layer 3 with a thickness of $0.2 \mu\text{m}$ was

formed by adopting a galvanic plating process under the conditions consisting of a galvanic plating current of 0.8A, a temperature of 70 °C and the galvanic plating time of 2min.

[00154] Example 14

[00155] The example aimed to prepare a pure gold article with the method of the present disclosure.

[00156] A gold article was prepared according to the same method as that in Example 1, except that a transparent film layer 4 was formed on the surface of the physical vapor deposition layer 2.

[00157] The pure gold having a surface plated with the physical vapor deposition layer 2 was placed in a vacuum furnace, and subjected to film plating by adopting a vacuum evaporation plating mode. The vacuum degree was adjusted to 2.0×10^{-2} Pa, the argon gas was injected with a gas flow of 60sccm; the vacuum degree was adjusted to 1.5×10^0 Pa, the glow cleaning was performed for 180s, the oxygen gas was injected with a gas flow of 80sccm, the vacuum degree was adjusted to 4.0×10^{-1} Pa, the aluminum target and the silicon target were activated and operated for 90s and 180s respectively, the power sources of the aluminum target and the silicon target were then shut off; the power supply of the evaporation source was activated, the AF pill was subjected to evaporation for 180s under the condition that the current of the evaporation source was 720A; then subjected to evaporating for 180s under the condition that the current

of the evaporation source was 780A; and subsequently subjected to evaporation for 420s under the condition that the current of the evaporation source was 850A, thereby forming a fluoride transparent film layer 4 having a thickness of 0.05 μ m.

[00158] Example 15

[00159] The gold article was prepared according to the same method as that in Example 1, except that the surface roughness of the pure gold was 10 μ m.

[00160] Example 16

[00161] The gold article was prepared according to the same method as that in Example 1, except that the surface roughness of the pure gold was 1 μ m.

[00162] Example 17

[00163] The gold article was prepared according to the same method as that in Example 1, except that the pure gold was subjected to ultrasonic cleaning at the ultrasonic frequency condition of 5kHz for 10 min.

[00164] Example 18

[00165] A gold article was prepared as in Example 1, except that the pure gold was cleaned by ultrasonic cleaning at 50kHz for 10 min.

[00166] Example 19

[00167] A gold article was prepared as in example 1, except that the cleaned and washed pure gold was not subjected to the baking treatment.

[00168] Comparative example 1

[00169] The gold article was prepared according to the same method as that in Example 1, except that the pure gold was subjected to a copper plating treatment under the conditions consisting of a copper-containing plating solution having a pH of 0.1, a plating temperature of 25 °C and a cathode current density of 4A/dm², and a plating time of 1 hour, thereby forming a copper layer with a thickness of 30μm on the pure gold surface.

[00170] Comparative example 2

[00171] The gold article was prepared according to the same method as that in Example 1, except that the aluminum alloy was used as the base, the aluminum alloy was subjected to film plating by means of the physical vapor deposition.

[00172] The precious metal articles obtained in Examples 1-19 and Comparative Examples 1-2 were subjected to performance tests, and the specific test results were shown in Table 1.

[00173] Table 1

Numbers	Glossiness/GU	Abrasion resistance/N
Example 1	853	18.4
Example 2	851	18.8
Example 3	842	20.2
Example 4	821	19.1
Example 5	816	19.9
Example 6	879	17.5
Example 7	865	20.9
Example 8	820	18.5

Example 9	816	20.6
Example 10	812	19.7
Example 11	854	20.2
Example 12	943	26.4
Example 13	895	24.3
Example 14	917	22
Example 15	719	19.4
Example 16	735	18.9
Example 17	754	17.8
Example 18	741	16.4
Example 19	792	16.8
Comparative example1	489	13.8
Comparative example2	762	15.2

[00174] As illustrated in the results of Table 1, the gold articles formed by using PVD to generate plating layer on the surface of the gold article base in the present disclosure exhibits desirable surface glossiness, and the formed plating layer is stable and is not prone to fall off. The gold article prepared with the method has thin film layer formed on the surface and can present diverse colors.

[00175] Examples 20-22

[00176] The precious metal articles were prepared according to same methods of Examples 1-3, respectively, except that the precious metal substrate was 925 silver having a purity of 92.5%, and the specific performance results were shown in Table 2.

[00177] Table 2

Numbers	Film color	Glossiness/GU	Abrasion resistance/N
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Example 20 (the precious metal substrate is silver)	Coffee	855	18.5
Example 21 (the precious metal substrate is silver)	Grey black	851	18.8
Example 22 (the precious metal substrate is silver)	Black	840	19.9

[00178] As can be seen from the above data, if silver is used as the precious metal substrate, the plating layer may be formed on the surface of silver by physical vapor deposition under the above conditions, the produced precious metal article can exhibit diverse colors and can be kept for a long time without fading.

[00179] The above content describes in detail the preferred embodiments of the present disclosure, but the present disclosure is not limited thereto. A variety of simple modifications can be made in regard to the technical solutions of the present disclosure within the scope of the technical concept of the present disclosure, including a combination of individual technical features in any other suitable manner, such simple modifications and combinations thereof shall also be regarded as the content disclosed by the present disclosure, each of them falls into the protection scope of the present disclosure.

Claims

1. A precious metal article comprising a precious metal substrate(1) and a physical vapor deposition layer(2) and a transparent film layer (4) which are sequentially attached to a surface of the precious metal substrate(1), and the transparent film layer (4) formed on the surface of the physical vapor deposition layer (2); wherein the precious metal is gold or silver, wherein the material of the transparent film layer (4) is a fluoride.

2. The precious metal article of claim 1, wherein the precious metal substrate(1) has a gold content of 33-99.99 wt%, preferably 75-99.99wt%, or the precious metal substrate (1) has a silver content of 92.5-99wt%.

3. The precious metal article of claim 1 or 2, wherein the thickness of the physical vapor deposition layer (2) is within a range of 10nm-50um, preferably 0.04um-2um; the material of the physical vapor deposition layer (2) is one or more selected from the group consisting of Ni, Ti, Zn, Cr, Mg, Nb, Sn, Al, In, Fe, Zr, Si, Cu, Ta, Ge, Ag, Co, Au, Gd, La, Y, Ce, W, Hf, Mo, CrN, TiN, TiAlCN, TiCN, TiAlN, AlTiN, TiB₂, ZrN, FeCo, AlSi, TiSi, CrSi, ZnAl, TiZn, TiAl, TiZr, TiSi, TiNi, NiAl, NiV, NiFe, gold-copper alloy and diamond-like carbon (DLC), and preferably gold-copper alloy.

4. The precious metal article of claim 1 or 2, wherein the precious metal substrate(1) has a surface roughness of 0.001um-50um, preferably 0.005um-0.2um.

5. A method of preparing a precious metal article of any one of claims 1-4 comprising the following step: attaching the physical vapor deposition layer

(2) to a surface of the precious metal substrate(1) by physical vapor deposition.

6. The method of claim 5, wherein the conditions of physical vapor deposition cause that the physical vapor deposition layer (2) has a thickness within a range of 10nm-50um.

7. The method of claim 5, wherein the physical vapor deposition mode is vacuum evaporation plating, vacuum sputtering coating or vacuum ion plating, preferably vacuum ion plating.

8. The method of claim 5, wherein the method further comprises a step of subjecting the surface of the precious metal substrate(1) to a surface treatment, such that the precious metal substrate (1) has a surface roughness within a range of 0.001um-50um, preferably 0.005um-0.2um.

9. The method of claim 8, wherein the method further comprises rinsing the surface-treated precious metal substrate(1) by means of the following modes: ultrasonically washing the precious metal substrate(1) under the ultrasonic frequency condition of 20-30kHz for 1-15min, and/or cleaning a surface of the precious metal substrate(1) with 95-98 wt% of alcohol.

10. The method of claim 9, wherein the method further comprises a step of baking the ultrasonically treated precious metal substrate(1), the baking temperature is 100-150°C, and the baking time is 5-30min.