

PROCESS FOR MANUFACTURING ORNAMENTAL PARTS
BY ION PLATING APPARATUS

1. Field of the Invention

5 This invention relates to a process for manufacturing ornamental parts having a color similar to that of gold and offering excellent resistance to corrosion and wear.

2. Background of the Invention

10 When a wear-resistant film is coated on surfaces of ornamental parts such as watch cases and metal spectacle frames, a dry process of ion plating has been used, instead of a wet process of electrochemical plating. The ion plating process permits coating not only metals such as Ni, Pd and Au but also compounds such as carbide and
15 nitride. Especially, a titanium nitride film coated by ion plating exhibits a simulated gold color and excellent corrosion and wear resistance. Therefore, it has been in wide use for a process for manufacturing ornamental parts. The improvements thereon is described in United
20 States Patent No. 4,226,082. However, the titanium nitride film exhibits pale yellow or pale ocher, which is not a necessarily preferable color for ornamental parts.

It is, therefore, proposed to overcoat an extremely thin gold film on the surface of the titanium nitride film so as to produce a vivid color as a whole (see United Kingdom Patent No. 2,000,812B). In this disclosure, the affinity at the interface between the titanium nitride film and the gold film, and the color reproducibility are of importance for the manufacturing technologies. But, the conventional processes are unsatisfactory in these respects.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a process and apparatus for producing coatings that exhibit a vivid gold-color and offer excellent corrosion and wear resistance, on surfaces of ornamental parts such as watch cases, metal spectacle frames, lighters, and pen caps.

According to this invention there is provided a process for manufacturing an ornamental part comprising:

providing within a vacuum chamber filled with a low-pressure gas atmosphere including nitrogen gas, the ornamental part as a work to be treated, an electron beam melting vapor source for evaporating titanium, and one or more sputtering vapor sources for supplying at least a gold vapor;

establishing an electric field between said ornamental part and said electron beam melting vapor source to produce a plasma glow discharge therebetween;

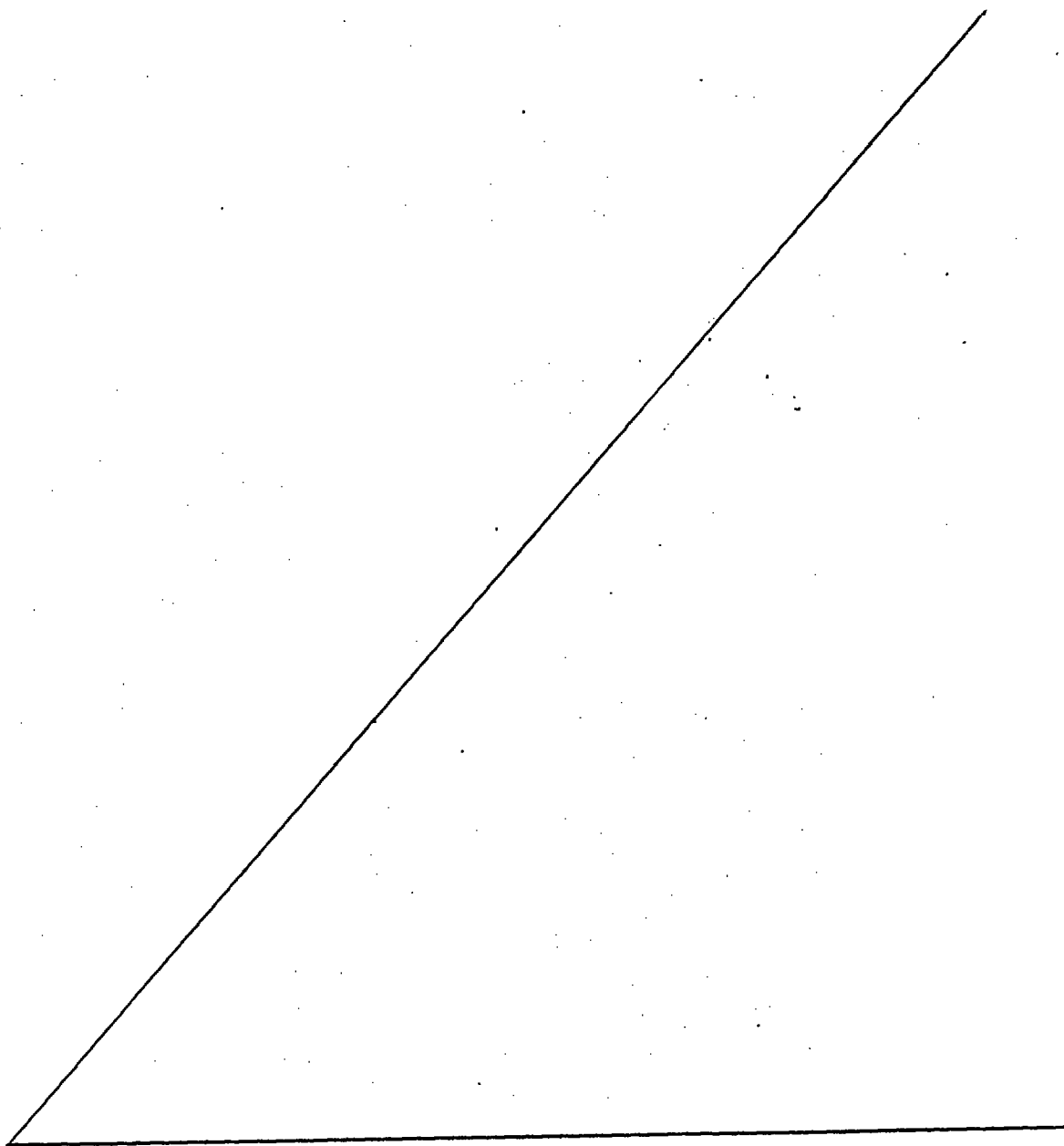
evaporating and ionizing the titanium in the plasma glow discharge to coat a film mainly composed of titanium nitride on a surface of said ornamental part;

at the final stage of this process, applying a negative voltage to one or more targets of said one or more sputtering vapor sources and at the same time, supplying the gold vapor to form a transition layer including both titanium nitride and gold; and

while continuing to supply the gold vapor, gradually stopping the evaporation of the titanium to coat a film of gold as a topcoat layer.

Preferably said film mainly composed of titanium nitride is from 1 to 10 microns in thickness, the film containing gold is from 0.1 to 1 micron in thickness, and the transition layer is 10 to 90% of the latter in thickness.

- 5 The process of this invention may be applied to a watch case, a metal spectacle frame, a lighter, or a pen cap.



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This invention will now be explained by way of example with reference to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view of an ion plating apparatus
5 for use in this invention;

Fig. 2 is a sectional view of a conventional filament type electron beam melting vapor source used in the ion plating apparatus used for this invention;

Fig. 3 is a sectional view of a conventional magnetron
10 type sputtering vapor source used in the ion plating apparatus for this invention;

Fig. 4 is a time chart showing a vapor supplying rate of Ti and Au obtained in the manufacturing process of this invention;

15 Fig. 5 is a profile showing the atomic composition of a coating film produced in the manufacturing process of this invention;

Fig. 6 is a sectional view of another ion plating apparatus which may be used for this invention; and

20 Fig. 7 is a conventional hollow cathode type electron beam melting vapor source used in the ion plating apparatus for this invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be explained by the following
25 examples with reference to the drawings:

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Example I

Referring to Fig. 1, there is shown an ion plating apparatus 100 used for this invention. _____

Within a vacuum chamber 101 having a gas inlet pipe 103 and an evacuation duct 102, there are arranged a rotary work holder 104 rotated around a vertical axis, a filament type electron beam melting vapor source 120, and a sputtering vapor source 130.

Fig. 2 shows in detail the filament type electron beam melting vapor source 120, in which a filament 122 is heated by a filament power source 123, and a high negative voltage is applied thereto by an electron beam power source 124. An electron beam 127 emitted from the filament 122 is then deflected in a magnetic field established by a magnet 126, and melts and vaporizes a melting material 121 loaded in a hearth 125. In this case, the vapor supplying rate depends on the temperature of molten material.

Fig. 3 shows in detail the sputtering vapor source 130, in which a target 131 is mounted on a cooling box 133 having magnets 132 internally. The cooling box 133 is protected by a grounded cover 134. Reference number 135 denotes an insulator. When a negative voltage is applied to the target 131 by means of the sputtering power source 136, positively charged gas ions in the vacuum chamber collide with the target 131, and atoms of the target material are sputtered in vaporized form having high kinetic energy. The sputtering

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vapor source shown in Fig. 3 is called a magnetron type one and provides high sputtering efficiency by the action of the magnetic field established by the magnets 132. The vapor supplying rate obtained when the sputtering vapor source is used does not depend upon the target temperature but is determined by the applied negative voltage and positive gas ion pressure.

Returning now to Fig. 1, the embodiment will be explained:

10 Watch cases 105 made of stainless steel (AISI 304) were mounted on the rotary work holder 104. On the electron beam melting vapor source 120 was loaded pure titanium as the melting material 121, and on the sputtering vapor source 130 was set a pure gold plate
15 as the target 131. While the vacuum chamber 101 was evacuated through the evacuation duct 102, a mixed gas of nitrogen and argon ($10\% \text{ N}_2 + 90\% \text{ Ar}$) was introduced from the gas inlet pipe 103 to a pressure of 8×10^{-4} Torr. Next, when a voltage of -1 kV was
20 applied by means of a discharge power source 106 through the rotary work holder 104, the vacuum chamber 101 was filled with a violaceous glow discharge plasma. Under these conditions, by driving the filament power source 123, the filament 122 is heated, and further
25 by driving the electron beam power source 124, the melting material 121 of titanium melted and the titanium vapor was supplied from the electron beam

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melting vapor source 120. Then, the titanium vapor was ionized in the plasma and further reacted with nitrogen ions. The resultant titanium nitride (TiN) began to deposit on the surfaces of the cases 105. Next, when
5 a negative voltage was applied by means of the sputtering power source 136 to the target 131 of gold plate, gold vapor was supplied by sputtering, and then gold films were coated on the TiN layers of the surfaces of the cases 105.

Fig. 4 shows schematically the supplying rates of
10 titanium and gold vapors in the above embodiment. Of the coating period of 25 minutes in total, for the first 20 minutes, the titanium vapor was supplied and for the second 10 minutes; the gold vapor was supplied. Thus, the first and second supplying periods partly overlap.
15 The atomic composition thus coated was analyzed by Auger electron spectroscopy. The result is shown in a profile of Fig. 5.

Of a coating about 1μ thick, the lower layer on the base material was mainly composed of titanium
20 nitride and the upper layer was mainly composed of gold. At the interface therebetween, a transition layer of about 65μ was present, in which the composition continuously varied.

In this invention it is the presence of this
25 transition layer which increases the affinity at the interface and enhances the coating durability.

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Example II

As in Example I, titanium nitride in thicknesses of 3 to 20 μ was coated on the surfaces of mirror-polished samples of stainless steel, and their surface conditions were observed. The result is shown in Table 1.

Table 1

Sample No.	TiN film thickness (μ)	Surface condition
1	3	Luster kept
2	5	"
3	8	"
4	10	"
5	12	Luster lost
6	15	"
7	18	"
8	20	"

From the result of Table 1, it is noted that when the coating thickness of TiN layer is within 10 μ , the base luster is kept.

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Next, with the layer including TiN kept 5 μ in thickness, gold layers were coated in thicknesses of 0.1 to 2 μ , as in Example I. In this example, the thicknesses of transient layers were variously changed. Colors of these samples and the result of a wear-resistant test are shown in Table 2. As the testing machine for the wear-resistant test, the Model 503 of TELEDYNE TABER, U.S.A. was used, in which the wheel (CS-100) was rotated ten times under a load of 500g to check if scratches were present.

Table 2

Base material	Layer including TiN		Transition layer		Layer including Au	
15						
	Sample No.	Layer including TiN (μ)	Transiti-on layer (μμ)	Layer including Au (μμ)	Color tone*	Wear resis-tant test*
20	11	5	0	100	b	z
	12	"	20	100	b	x
	13	"	65	100	c	x
	14	"	0	300	a	z
	15	"	50	300	a	x
25	16	"	250	300	c	x
	17	"	50	500	a	x
	18	"	200	500	a	x
	19	"	400	500	b	x
	20	"	0	1000	a	y, z

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5	21	"	100	1000	a	y
	22	"	500	1000	a	x
	23	"	900	1000	b	x
	24	"	1000	1500	a	y
	25	"	1400	1500	b	y
	26	"	1000	2000	a	y
	27	"	1500	2000	a	y

- 10 * a ... vivid gold
 b ... gold
 c ... pale gold
 x ... scratch observed
 y ... no scratch observed
15 z ... peeling occurred

The result shown in Table 2 leads to the following conclusion:

- (1) Where the transient layer is not substantially
20 present (Sample Nos. 11, 14 and 20), peeling
occurs, but where the transient layer occupies
10 to 90% of the thickness of the layer including
gold, no peeling occurs.
- (2) Even if the layer including gold is only 100 mu
25 thick, a gold color is produced, but when it is
coated in thicknesses of 300 mu or more, a vivid
gold color is produced.

- (3) When the layer including gold exceeds 1000 mμ,
i.e. 1 μ, it is easy to scratch.

Example III

Watch cases made of brass electroplated with nickel and chrome were used as works to be treated (105 in Fig. 1). Utilizing the ion plating apparatus shown in Fig. 1, a layer including TiN and a layer including Au were coated through the same process as in Example I. In this Example III, a titanium alloy (80% Ti, 10% Zr, 10 and 10% Hf) was used as a melting material (121 in Fig. 1), instead of pure titanium, and an Au alloy plate (84% Au, 10% Pd, and 6% Cu) was used as a sputtering target (131 in Fig. 1), instead of a pure gold plate.

- 15 The resultant 3μ-thick layer including TiN was composed of a complex nitride layer including TiN, ZrN and HfN, and the 300 mμ-thick layer including gold was composed of an Au-Pd-Cu alloy having the substantially same composition as that of the target (131 in Fig. 1). The
20 thickness of the transient layer was about 100 mμ. The complex nitride layer is superior in the affinity with the base to a simple TiN layer, where the base is composed of brass electroplated with nickel and brass. Also, the layer composed of an Au-Pd-Cu alloy exhibited an
25 elegant color, generally called pink gold or rose gold.

Example IV

Another embodiment of an ion plating apparatus used in this invention is shown in Fig. 6. In this apparatus 200, within the vacuum chamber 201 having a gas inlet pipe 203 and an evacuation duct 202, there are arranged a rotary work holder 204 rotated around a horizontal axis by rollers 206, a hollow cathode type electron beam melting vapor source 220, and a plurality of sputtering vapor sources (230, 240 and 250).

10 Fig. 7 shows in detail the hollow cathode type electron beam melting vapor source 220. In this vapor source, a small amount of argon gas was introduced into the hollow cathode 222 made of refractory metal through a gas inlet pipe 221. By means of a cathode power
15 source 225, a high negative voltage overlapping an rf voltage was applied. Within the hollow cathode 222, the argon gas was in the plasma condition. As the top of the cathode 222 was heated, an electron beam 226 was emitted toward a hearth 223. A melting material 224,
20 which was supplied continuously from the bottom of the hearth 223, melted at its top by means of the electron beam, thus producing vapor. This electron beam source has been recently developed and is known to provide very high efficiency.

Returning now to Fig. 6, this embodiment will be explained:

On the rotary work holder 204, watch cases 205 made of stainless steel were mounted as works to be treated.

5 In the hollow cathode type electron beam melting vapor source 220, pure titanium was loaded as a melting material 224. In the sputtering vapor sources 230, 240 and 250, a gold plate, a palladium plate, and a copper plate were set, respectively as targets 231,
10 241 and 251.

As in Example I, while exhausting the vacuum chamber 201 through the evacuation duct 202, from the gas inlet pipe 203, a mixed gas of nitrogen and argon was introduced and from the gas inlet pipe 221, an
15 argon gas was introduced to a pressure of 2×10^{-3} Torr. Next, a voltage of -800V was applied to the works 205 by means of a discharge power supply 261 through a sliding brush 207 and the rotary work holder 204. As a result, the vacuum chamber 201 was filled with
20 a violaceous glow discharge plasma. Under these conditions, by driving the cathode power source 262, a negative voltage was applied to the hollow cathode 222. Then, by the electron beam emitted from the cathode 222, the titanium melting material 224 was melted and
25 evaporated. This titanium vapor was ionized in the plasma and reacted with nitrogen ions in the plasma. The resultant titanium nitride was deposited on the surfaces of the cases 205.

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Next, by driving the sputtering power sources 263, 264 and 265, negative voltages were applied to the targets 231, 241 and 251. Then, the Au, Pd and Cu vapors were sputtered, and Au-Pd-Cu alloy layers were coated together
5 with TiN on the surfaces of the cases.

In this final process, by adjusting the negative voltages applied to the plurality of targets 231, 241 and 251, each of the Au, Pd and Cu vapor supplying rates can independently be controlled. Thus, according
10 to this example, the color of the Au-Pd-Cu alloy surface was successfully modulated arbitrarily from light pink gold to deep pink gold with good reproducibility.

One of the features of the manufacturing process of the invention is that the vapor of titanium
15 ——— is supplied from the electron beam melting vapor source, while the vapor of gold is supplied ——— from the sputtering vapor source.

In order to evaporate high melting point titanium, the electron beam melting vapor source has been used
20 from the past. On the other hand, as a vapor source of gold which easily melts, an electron beam melting vapor source, a resistance heat melting vapor source using a tungsten board, or an rf induction melting vapor source has generally been used. In distinction, the present
25 invention uses a sputtering vapor source having a relatively low vapor supplying rate.

Such a sputtering vapor source has the following advantages when used in this invention:

First, the sputtering vapor source depends for its supplying rate upon the negative voltage applied to the target and the positive gas ion pressure, and does not depend upon the temperature of molten material as in the melting type vapor source. Therefore, the vapor supplying rate can be changed with a good response.

10 Secondly, when an alloy of a plurality of elements is evaporated, the vapor composition does not shift by the difference among the vapor pressure of particular element in thermal equilibrium, as in the melting type vapor source. Therefore, it is possible to supply the
15 vapor of the substantially same composition as the alloy which forms the target.

The sputtering vapor source having the above features is essential in order to control the thickness of the transient layer and further to modulate the color
20 of the gold based topcoat film with good reproducibility in the manufacturing process of the invention.



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CLAIMS:

1. A process for manufacturing an ornamental part comprising:
providing within a vacuum chamber filled with a low-pressure gas atmosphere including nitrogen gas, the ornamental part as a work to be treated, an electron beam melting vapor source for evaporating titanium,
5 and one or more sputtering vapor sources for supplying at least a gold vapor;
establishing an electric field between said ornamental part and said electron beam melting vapor source to produce a plasma glow discharge therebetween;
10 evaporating and ionizing the titanium in the plasma glow discharge to coat a film mainly composed of titanium nitride on a surface of said ornamental part;
at the final stage of this process, applying a negative voltage to one or more targets of said one or more sputtering vapor sources and at
15 the same time, supplying the gold vapor to form a transition layer including both titanium nitride and gold; and
while continuing to supply the gold vapor, gradually stopping the evaporation of the titanium to coat a film of gold as a topcoat layer.
2. A process as claimed in claim 1, wherein said titanium comprises
20 pure titanium.
3. A process as claimed in claim 1, wherein said titanium comprises a titanium alloy with zirconium and hafnium.
4. A process as claimed in any preceding claim, wherein said sputtering target comprises a gold alloy with palladium and copper.
- 25 5. A process as claimed in any of claims 1 to 3, wherein one of said plurality of targets comprises gold.
6. A process as claimed in any preceding claim, wherein said low-pressure gas comprises nitrogen and argon.



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7. A process as claimed in claim 1, wherein said film mainly composed of titanium nitride is from 1 to 10 microns in thickness, the film containing gold is from 0.1 to 1 micron in thickness, and the transition layer is 10 to 90% of the latter in thickness.
- 5 8. A process as claimed in any preceding claim, wherein said ornamental part is one of a watch case, a metal spectacle frame, a lighter, or a pen cap.
9. A process as claimed in any preceding claim, wherein said electron beam melting vapor source is of a filament type.
- 10 10. A process as claimed in any of claims 1 to 8, wherein said electron beam melting vapor source is of a hollow cathode type.
11. A process as claimed in any preceding claim, wherein said sputtering vapor source or sources are of a magnetron type.
12. A process as claimed in any preceding claim, wherein the work to
15 be treated is mounted on a rotary work holder having a vertically pivoted rotation axis.
13. A process as claimed in any of claims 1 to 11, wherein the work to be treated is mounted on a work holder having a horizontally pivoted rotation axis.
- 20 14. A manufacturing process substantially as herein described with reference to and as illustrated in the accompanying drawings.
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