

obtained gold layer was examined under various lighting conditions and the details of the colour tone examinations are given in Figure 1 which shows the reflection ratios of the gold layer against the wave length of the light. These data are the measurement results obtained on mirror-finished surfaces: Curve (1) shows the colour tone of TiN, Curve (2) shows the colour tone of pure gold, Curve 3 shows the colour tone of a gold layer having a thickness of about 300Å (0.03 µm) and Curve (4) shows the colour tone of a gold layer having a thickness of 1000Å (0.1 µm). It will be seen that as the gold layer increases in thickness, the colour tone of the gold layer more and more approximates to that of pure gold. Thus, as is clear from Figure 1, the gold layer attains the colour tone approaching that of pure gold. As far as the colour tone is concerned, it is clear that a gold layer having a quite small thickness has a colour tone almost the same as that of pure gold. If the functional aspect such as corrosion resistance is satisfied with an externally ornamental part covered with the coating which includes a quite thin gold layer, coated external ornamental part substantially equal to a pure gold externally ornamental part is obtained by use of a quite thin gold layer. In Example 1, since the substrate material is stainless steel which has a corrosion resistance and the TiN layer is hard and has a yellow colour similar to the colour tone of pure gold, even when the top gold layer wears away, the gold-like colour tone of the external ornamental part will not be affected by such wearing of the top gold layer to thereby provide an externally ornamental part which has a golden colour tone and which exhibits excellent corrosion resistance and wear resistance properties. As the thickness of the top gold layer varies from 100Å (0.01 µm) to 1 µm, the colour tone of the part varies accordingly and the colour tone of the part also varies by forming the top layer with an alloy of gold and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti. In this way, externally ornamental parts having various golden colour tones within a wide range are obtainable.

Example 2

A brass wrist watch case is coated with nickel and chromium in that order by electrochemical plating. Thereafter, the watch case is placed into the ion plating system and then coated with TiN and Au by the same process as employed in Example 1. Although brass itself has insufficient corrosion resistance to be used as the material for an externally ornamental part, when the brass part is coated with nickel and then chromium, the corrosion resistance of the brass part is enhanced. Since a hard and yellow TiN layer is deposited on the chromium layer even if the topmost gold layer wears away, the produced externally ornamental part will not lose its fine golden colour tone to thereby provide a wrist watch case having the desired properties called for such a part.

Example 3

A stainless steel wrist watch case is washed with an organic solvent and then placed into an ion plating system. The ion plating system is evacuated

introduced into the ion plating system to adjust the pressure to 5×10^{-3} Torr. Thereafter, the wrist watch case within the ion plating system has a D.C. voltage of 1 KV applied thereto to bombard the case and then the plating system is evacuated being followed by introduction of nitrogen gas into the system to attain the pressure of 5×10^{-3} Torr.

Under this pressure, Ti is vaporised by electron beam heating and reacts with nitrogen gas in the atmosphere of plasma generated by thermal electrons emitted by the filament of the ion plating system to form a yellowish titanium nitride layer on the wrist watch case. After 10 minutes, copper which is previously located in a boat within the ion plating system is vaporised by resistance heating during formation of the titanium nitride layer so as to impregnate the titanium nitride layer with the copper. After a reactive ion plating is performed lasting 10 minutes, the copper-impregnated titanium nitride layer is formed. During the reactive ion plating, power to the boat is adjusted to maintain the copper evaporation amount per unit time constant. Thus, a wrist watch case is produced which presents a fine light reddish golden colour tone different from the greenish colour tone of the prior art wrist watch case which has the titanium nitride layer alone. The colour tone of the thus produced wrist watch case was examined under various lighting conditions and the results of the examination are given in Figure 2. Figure 2 shows the wave length to reflection ratios and the samples employed in these examinations had mirror finish surfaces. In Figure 2, Curve (1) is the colour tone of the prior art titanium nitride layer, Curve (2) is the colour tone of pure gold and Curve (3) is the colour tone of a titanium nitride layer containing 20% of copper. The examination showed that the colour tone of the copper-containing titanium nitride layer was reddish golden.

In this example, since the stainless steel of the substrate exhibits excellent corrosion resistance and the titanium nitride exhibits excellent wear resistance and is hard, a less expensive golden colour tone wrist watch case having excellent properties can be obtained without being substantially affected by the copper contained in the titanium nitride layer. When the concentration of the copper in the titanium nitride layer is varied, the golden colour tone which is obtained also varies accordingly. It has been found that a copper concentration of up to 50% can be used without adversely affecting the corrosion resistance and wear resistance properties of the obtained product.

Example 4

A brass wrist watch case is coated with nickel and chromium in that order by electrochemical plating. Thereafter, a titanium nitride layer is deposited on the chromium layer by reactive ion plating in the same manner as employed in connection with Example 3 and then the titanium nitride layer is impregnated with silver. Although brass has insufficient corrosion resistance for an external part substrate material when the metal is employed alone, by depositing the nickel and chromium layers on the brass substrate, the corrosion resistance of the brass substrate is improved. Since a hard

titanium nitride layer of golden colour is further deposited on the chromium layer, a wrist watch case having excellent properties can be provided.

As compared with stainless steel, since brass is worked easily, this metal is employed for producing a part having a design which requires a rather complicated process. When silver is contained in the outer surface area of the titanium nitride layer, the spectre reflection ratio represented by Curve (4) in Figure 2 is obtained to provide a whitish golden colour tone.

In the examples described hereinabove, although description has been made of instances in which the substrate is formed of stainless steel or brass, the substrate may be also formed of other metals such as copper alloys and aluminium alloys which are conventionally employed for the substrate material for externally ornamental parts without departing from the scope of the invention. When they are considered to have sufficient thermal resistance, ceramics and plastics materials may also be employed as the substrate and the use of such nonmetals also provide the same effects as those obtainable by the metals. As the material for the underlying yellowish layer which have the same effects as those of TiN, TaN, TaC, ZrN and VN may be employed within the scope of the present invention.

In the examples described hereinabove, gold, copper or silver is impregnated in the titanium nitride but since external ornamental parts such as wrist watch cases and bands are required to have varying colour tones because fashions vary at different times and at different regions throughout the world, by impregnating the titanium nitride layer with at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir and Pt and maintaining the ratio of light reflectance within the range of 1.2 : 1 to 3.0 : 1 at 550 m μ and 400 m μ on the surface of the coating, it is possible to meet such varying colour tone requirement.

Since the colour tone of an externally ornamental part is determined by the absorption and reflection properties in the thickness of the coating from the outer surface for a depth of less than 1 μ m, it is only necessary to distribute the metal or metals to be impregnated in the titanium nitride layer within the outer surface of the coatings. Alternatively, such impregnation metal or metals may be distributed throughout the thickness of the titanium nitride layer in order to make manufacture processes more uniform. The thermal treatment after the formation of the coating layer has effects on the colour tone and stabilises the layer. The TiN, TaN, TaC, ZrN and VN layer may be formed by not only ion plating, but also by sputtering or CVD.

The thickness of the titanium nitride layer extending from the outer surface of the coating towards the substrate for up to 1 μ m may be impregnated with at least one member selected from the group comprising Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sb, Ti, Hf, Ta, W, Ir, Pt and Au by vacuum deposition or sputtering other than the procedures described in connection with the various examples.

In alternative embodiments of the invention, the coating comprises a titanium nitride phase adjacent to the substrate, an intermediate mixture phase of titanium nitride and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au on the side of the titanium nitride phase remote from the substrate and an outermost phase comprising Au or an alloy phase of Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti.

In a still further embodiment of the invention, an article has a coating comprising an innermost Ti phase adjacent to said substrate, a first TiN phase on the side of the Ti phase remote from the substrate, a second intermediate mixture or an alloy phase on the TiN phase and comprising TiN and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au and an outermost mixture or an alloy phase on said second intermediate or alloy phase and comprising Au or an alloy of Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti, the components in each phase gradually merging into the adjacent phase or phases.

CLAIMS

1. An article as herein defined, the external surface of which is of a golden colour, the article comprising a thermal resistant substrate and the surface being provided by a coating principally of a material selected from TiN, TaN, TaC, ZrN and VN deposited on the substrate and wherein the applied coating has been further coated with at least one additive metal selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au so as to give at the entire outer surface of the article a layer of not more than 1 μ thickness comprising said additive metal and so as to give at the outer surface of the coating a ratio of light reflectance at 550 m μ to that at 400 m μ of from 1.2 : 1 to 3.0 : 1.

2. An article as claimed in claim 1, in which the coating comprises a mixture phase of titanium nitride and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au and at the outer surface of the coating the ratio of light reflectance at 500 m μ to that at 400 m μ is from 1.2 : 1 to 3.0 : 1.

3. An article as claimed in claim 1, in which said coating has a titanium nitride phase adjacent to the substrate and a second phase on the side of the titanium nitride phase remote from the substrate, said second phase comprising Au or Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti.

4. An article as claimed in claim 1, in which the coating comprises a titanium nitride phase adjacent to the substrate, an intermediate mixture phase of titanium nitride and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt



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titanium nitride layer of golden colour is further deposited on the chromium layer, a wrist watch case having excellent properties can be provided.

As compared with stainless steel, since brass is worked easily, this metal is employed for producing a part having a design which requires a rather complicated process. When silver is contained in the outer surface area of the titanium nitride layer, the spectoreflexion ratio represented by Curve (4) in Figure 2 is obtained to provide a whitish golden colour tone.

In the examples described hereinabove, although description has been made of instances in which the substrate is formed of stainless steel or brass, the substrate may be also formed of other metals such as copper alloys and aluminium alloys which are conventionally employed for the substrate material for externally ornamental parts without departing from the scope of the invention. When they are considered to have sufficient thermal resistance, ceramics and plastics materials may also be employed as the substrate and the use of such nonmetals also provide the same effects as those obtainable by the metals. As the material for the underlying yellowish layer which have the same effects as those of TiN, TaN, TaC, ZrN and VN may be employed within the scope of the present invention.

In the examples described hereinabove, gold, copper or silver is impregnated in the titanium nitride but since external ornamental parts such as wrist watch cases and bands are required to have varying colour tones because fashions vary at different times and at different regions throughout the world, by impregnating the titanium nitride layer with at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir and Pt and maintaining the ratio of light reflectance within the range of 1.2 : 1 to 3.0 : 1 at 550 m μ and 400 m μ on the surface of the coating, it is possible to meet such varying colour tone requirement.

Since the colour tone of an externally ornamental part is determined by the absorption and reflection properties in the thickness of the coating from the outer surface for a depth of less than 1 μ m, it is only necessary to distribute the metal or metals to be impregnated in the titanium nitride layer within the outer surface of the coatings. Alternatively, such impregnation metal or metals may be distributed throughout the thickness of the titanium nitride layer in order to make manufacture processes more uniform. The thermal treatment after the formation of the coating layer has effects on the colour tone and stabilises the layer. The TiN, TaN, TaC, ZrN and VN layer may be formed by not only ion plating, but also by sputtering or CVD.

The thickness of the titanium nitride layer extending from the outer surface of the coating towards the substrate for up to 1 μ m may be impregnated with at least one member selected from the group comprising Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sb, Ti, Hf, Ta, W, Ir, Pt and Au by vacuum deposition or sputtering other than the procedures described in connection with the various examples.

In alternative embodiments of the invention, the coating comprises a titanium nitride phase adjacent to the substrate, an intermediate mixture phase of titanium nitride and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au on the side of the titanium nitride phase remote from the substrate and an outermost phase comprising Au or an alloy phase of Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti.

In a still further embodiment of the invention, an article has a coating comprising an innermost Ti phase adjacent to said substrate, a first TiN phase on the side of the Ti phase remote from the substrate, a second intermediate mixture or an alloy phase on the TiN phase and comprising TiN and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au and an outermost mixture or an alloy phase on said second intermediate or alloy phase and comprising Au or an alloy of Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti, the components in each phase gradually merging into the adjacent phase or phases.

CLAIMS

1. An article as herein defined, the external surface of which is of a golden colour, the article comprising a thermal resistant substrate and the surface being provided by a coating principally of a material selected from TiN, TaN, TaC, ZrN and VN deposited on the substrate and wherein the applied coating has been further coated with at least one additive metal selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au so as to give at the entire outer surface of the article a layer of not more than 1 μ thickness comprising said additive metal and so as to give at the outer surface of the coating a ratio of light reflectance at 550 m μ to that at 400 m μ of from 1.2 : 1 to 3.0 : 1.

2. An article as claimed in claim 1, in which the coating comprises a mixture phase of titanium nitride and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au and at the outer surface of the coating the ratio of light reflectance at 500 m μ to that at 400 m μ is from 1.2 : 1 to 3.0 : 1.

3. An article as claimed in claim 1, in which said coating has a titanium nitride phase adjacent to the substrate and a second phase on the side of the titanium nitride phase remote from the substrate, said second phase comprising Au or Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti.

4. An article as claimed in claim 1, in which the coating comprises a titanium nitride phase adjacent to the substrate, an intermediate mixture phase of titanium nitride and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt



and Au on the side of the titanium nitride phase remote from the substrate and an outermost phase comprising Au or an alloy phase of Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd,

5 Ag, Cd, In, Sn and Ti.

5. An article as claimed in claim 1, in which the coating comprises an innermost Ti phase adjacent to said substrate, a first TiN phase on the side of the Ti phase remote from the substrate, a second

10 intermediate mixture or an alloy phase on the TiN phase and comprising TiN and at least one member selected from Al, Si, V, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Ti, Hf, Ta, W, Ir, Pt and Au and an outermost mixture or an alloy
15 phase on said second intermediate or alloy phase and comprising Au or an alloy of Au and at least one member selected from Al, Cr, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn and Ti, the components in each phase gradually merging into the adjacent phase or
20 phases.

6. An article as claimed in any preceding claim, in which the thermal resistant substrate is a material selected from steel, brass, nickel silver, aluminium alloy, copper alloy, ceramics and heat resistant

25 plastics material.

7. An article having an external surface of a golden colour substantially as hereinbefore described with reference to the specific examples.

8. An article as claimed in any preceding claim

30 and being in the form of a case or part of a case for a wrist watch or a strap for supporting a wrist watch.