

COLOURED GOLD ALLOY AND METHOD FOR FORMING THE SAME

FIELD OF INVENTION

The invention relates to coloured gold alloys and method for forming the
5 same. In particular, the invention relates to coloured gold alloys having titanium
content of more than 10 weight percent (wt%).

BACKGROUND TO THE INVENTION

The following discussion of the background to the invention is intended to
facilitate an understanding of the present invention. However, it should be
10 appreciated that the discussion is not an acknowledgment or admission that any
of the material referred to was published, known or part of the common general
knowledge in any jurisdiction as at the priority date of the application.

Gold jewellery and watches are common accessories not only for the status-
conscious, but also for the fashion-goers. Coloured gold alloys are becoming
15 increasingly high in demand compared to traditional yellowish gold. Such
colourings on gold alloys include maroon, blue, green or greenish-blue, and
black.

Current techniques for producing coloured gold alloys include electroplating,
chemical or physical vapour deposition, patination, and oxidation. Oxidation of
20 the gold alloy is presently the most commonly used technique to produce
coloured gold.

In a typical oxidation process, an alloy comprising gold and colouring
elements are heated in an oxidizing atmosphere at a temperature between
700°C and 950°C for 20 to 60 minutes. The resultant gold alloy is then cooled.
25 To improve the mechanical properties of the gold alloy, titanium is often included
as one of the alloying elements. The titanium-gold alloy possesses a coloured
surface due to the formation of an intermetallic phase within the bulk of the gold
alloy. However, as titanium is highly reactive even in ambient environment,

titanium oxide is formed at the surface of the gold alloy. Titanium oxide is brittle and deteriorates the mechanical properties of the gold alloys. Such oxide layers do not possess sufficient scratch resistance or durability for daily wear.

Protection of the oxide layers is therefore needed. Alternatively, little (less than 2
5 wt%) or no titanium is added as an alloying element. Mechanical properties of the resultant gold alloy is therefore compromised.

It is desirable to provide a coloured gold alloy that overcomes, or at least alleviates, the above problems. It is also desirable to provide a method for forming the coloured gold alloy, which method is simple and economical.

10 SUMMARY OF THE INVENTION

Throughout this document, unless otherwise indicated to the contrary, the terms "comprising", "consisting of", and the like, are to be construed as non-exhaustive, or in other words, as meaning "including, but not limited to".

In a first aspect of the present invention, there is provided a method for
15 forming coloured gold alloy. The method comprises coating a layer of oil on a gold alloy and heating the coated gold alloy at a temperature selected based on the colouring on the gold alloy desired until the colouring appears. The gold alloy comprises gold, titanium, and at least one other element. The titanium content in the alloy is more than 10 wt%.

20 In a second aspect of the present invention, there is provided a coloured gold alloy comprising gold, titanium, and at least one other element formed in accordance with the first aspect of the invention.

In a third aspect of the present invention, there is provided jewellery
25 comprising a coloured gold alloy comprising gold, titanium, and at least one other element formed in accordance with the first aspect of the invention.

In a fourth aspect of the present invention, there is provided the use of a coloured gold alloy in jewellery, the coloured gold alloy comprising gold, titanium, and at least one other element formed in accordance with the first aspect of the invention.

DETAILED DESCRIPTION

The invention relates to coloured gold alloys and method for forming the same. In particular, the invention relates to coloured gold alloys having titanium content of more than 10 weight percent (wt%).

5 In accordance with a first embodiment of the invention, there is provided a method for forming coloured gold alloys. The gold alloy preferably contains 58 - 85 wt% gold. This covers commercially termed 14 - 20 carat gold. Titanium forms one component of the alloy. Titanium is preferably present in at least 10 wt% of the gold alloy. Preferably, the titanium content does not exceed 50 wt%.

10 The balance of the gold alloy comprises at least one other element. The other element preferably aids in the machinability or castability of the resultant coloured gold alloy. More preferably, the other element acts as a deoxidizer, suppressing the formation of metallic oxides. Examples of the other element include the following:

- 15 • 0 – 8 wt% Fe
- 0 – 5 wt% Co
- 0 – 5 wt% Cr
- 0 – 5 wt% Mn
- 0 – 5 wt% Mo
- 20 • 0 – 5 wt% Pd
- 0 – 5 wt% Nb
- 0 – 5 wt% W
- 0 – 6 wt% Al
- 0 – 2 wt% Si.

25 A thin layer of oil is first coated on the gold alloy. Preferably, the thin layer of oil is coated on the entire exposed surface of the gold alloy. The thin layer of oil

includes, but not limited to, low viscosity oils such as olive oil, organic oil, lubricating oil, hydrocarbons. The coating of the thin layer of oil over the gold alloy helps to minimize formation of undesirable metallic oxides on the gold alloy. Otherwise, the presence of the oxides on the surface of the gold alloy will
5 cause poor surface finishing since oxides are brittle and give a rough-dimple surface appearance.

The coated gold alloy is then heated at a temperature selected based on the colouring on the gold alloy desired. The heating continues until the colouring appears. The gold alloy is heated at temperatures between 400 °C and 900 °C,
10 and in particular,

- 400 – 500 °C for maroon coloured gold alloy;
- 500 – 600 °C for blue coloured gold alloy;
- 650 – 700 °C for green and greenish-blue coloured gold alloy; and
- 800 – 900 °C for black coloured gold alloy.

15 As the heating temperature approaches the selected temperature, the desired colouring on the gold alloy starts to become visible. The gold alloy continues to be heated until the selected temperature is reached whereby the desired colouring starts to stabilize on the gold alloy.

In one embodiment, the gold alloy is heated in a non-oxidizing environment
20 such as a carburizing environment providing carbon precursors to form carbonaceous layer on the surface of the gold alloy. The carbonaceous layer may comprise carbides. Preferably, the gold alloy is heated using a carburizing flame consisting of an oxy-acetylene flame. The flame is preferably acetylene-rich oxy-acetylene flame. The carburizing flame is non-oxidizing. The carburizing
25 flame is neutral (i.e. $C_2H_2/O_2 = 1$) or reducing (i.e. $C_2H_2/O_2 > 1$), and more preferably reducing.

In an alternative embodiment, the gold alloy is heated in open air on a hot-plate or furnace. Other heating sources apparent to a person skilled in the art

are also suitable. After the desired colouring starts to stabilize on the gold alloy, heating is then immediately stopped. In one embodiment, the hot gold alloy is allowed to cool to room temperature in still air to obtain the coloured gold alloy.

5 In an alternative embodiment, the hot gold alloy is rapidly quenched in a quenching medium to obtain the coloured gold alloy. The gold alloy is preferably quenched at room temperature. In one embodiment, the quenching medium is a hydrocarbon medium. Preferably, the hydrocarbon medium is low viscosity oil. And more preferably, the low viscosity oil is one of olive oil, organic oil or lubricating oil, or a mixture thereof.

10 Examples

Example 1

Gold alloys are formed by conventional techniques such as electric arc melting. The desired compositions of the gold alloy are mixed and melted in an inert atmosphere or under vacuum pressure. For instance, for Alloy 2 (18 carat
15 gold) illustrated in Table 1 below, 75 wt% Au, 17 wt% Ti, 5 wt% Fe, 0.8 wt% Co, 0.5 wt% Cr, 1.5 wt% Al, and 0.2 wt% Si are mixed and melted in an induction argon atmosphere in a conventional crucible such as magnesium oxide crucible. The melting may also be conducted in a conventional electric arc furnace with a graphite crucible. Upon melting, the melted gold alloy flows into a casting mould
20 and cooled to form the desired shape. The cast gold alloy is subsequently grinded, polished and buffed to mirror-like finish so that the gold alloy surface is essentially contaminant-free. Other melting techniques and finishing steps are also suitable for obtaining an essentially contaminant-free gold alloy surface.

After the formation of gold alloy, the gold alloy is dipped into a bath of olive oil
25 to coat a thin layer of olive oil on the gold alloy. The gold alloy is next heated with an oxy-acetylene flame. The selected temperature is set at 400 °C to obtain a maroon coloured gold alloy. The ratio of the volumetric flow rates of acetylene to oxygen is carefully controlled such that the flame is carburizing. In this example, the ratio is kept at 5:3. Other ratios are also suitable as long as there is
30 excess acetylene in the flame.

The heating continues until a visible dull red or maroon appearance of the gold alloy is obtained. Heating is stopped at approximately 450 °C and the gold alloy is allowed to cool to room temperature in still air. A resultant maroon coloured gold alloy is obtained.

5 Example 2

The gold alloy in this example is formed in the same manner as described in Example 1 (i.e. Alloy 2). After the formation of gold alloy, the gold alloy is dipped into a bath of olive oil to coat a thin layer of olive oil on the gold alloy. The gold alloy is next heated on a hot-plate in open air. The selected temperature is set at
10 650 °C to produce greenish-blue coloured gold alloy.

As the heating temperature approaches 500 °C, the surface of the heated gold alloy gradually changes from maroon to slight bluish hue. As the temperature continues beyond 500 °C, the bluish hue becomes more visible and stable. As the heating temperature approaches 650 °C, the surface of the
15 heated gold alloy gradually changes from blue to greenish-blue. Heating is stopped at 650 °C and the gold alloy is allowed to cool to room temperature in still air. A resultant greenish-blue coloured gold alloy is obtained.

Example 3

The gold alloy in this example is formed in the same manner as described in
20 Example 1 (i.e. Alloy 2). After the formation of gold alloy, the gold alloy is dipped into a bath of olive oil to coat a thin layer of olive oil on the gold alloy. The gold alloy is next heated with an oxy-acetylene flame at 900°C. The ratio of the volumetric flow rates of acetylene to oxygen is carefully controlled such that the flame is carburizing. In this example, the ratio is kept at 5:3. Other ratios are also
25 suitable as long as there is excess acetylene in the flame.

The heating continues until a visible wetting appearance of the gold alloy is obtained. It takes approximately one minute at 900°C since heating begins for the visible wetting appearance to be observed. The gold alloy is immediately quenched in an olive oil bath container at room temperature. The bath container

contains olive oil approximately fifty times larger in volume than the volume of the gold alloy. The gold alloy, when totally immersed in the olive oil bath container, is at least 15 mm below the olive oil level. As the gold alloy is immersed in the olive oil bath, the high temperature may cause vapourization of the olive oil initially. Thus, the excess olive oil ensures there are sufficient carbon particles to form carbonaceous layer on the surface of the gold alloy. The olive oil bath container is exposed to air. Oxygen may be present at the olive oil surface. By having the gold alloy immersed at least 15 mm below the olive oil level, oxidation of the gold alloy is minimized. Further, any oxides inevitably formed on the gold alloy surface may be reduced. The gold alloy obtained in this manner is black in colour.

Table 1 illustrates the exemplary compositions of 14 – 20 carat gold alloy suitable for the working of the invention.

Element (wt%)	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5	Alloy 6	Alloy 7	Alloy 8	Alloy 9
Au	83.33	75	75	75	75	75	58.5	58.5	58.5
Ti	15.07	17	15	24.5	23	18	33.5	37	29
Fe	1.6	5	5	0.5		4.5	2.5	1	6
Co		0.8				0.5		0.3	1.2
Cr		0.5	1		0.5	1			
Mn			1		0.5	1			
Mo									
Pd			1		1			1	2
Nb			2						
W								0.5	
Al		1.5					5	1.5	3
Si		0.2					0.5	0.2	0.3

TABLE 1: Based on 999 Gold, 14 - 20 carat

During the heating of the gold alloy, for instance with a carburizing flame, a carbonaceous layer on the surface of the gold alloy is formed. There are three zones (inner, intermediate and outer) in operation in a carburizing flame. In the inner zone, acetylene reacts with oxygen to form carbon monoxide and
5 hydrogen. In the outer zone, carbon monoxide reacts with hydrogen and oxygen to form carbon dioxide and steam. In the intermediate zone, the excess acetylene results in free carbon particles, which cause the carburizing flame to be whitish. The carbon particles are deposited on the gold alloy surface and some of the carbon particles are partially dissolved within the metallic crystal
10 structure of the gold alloy. Some of the carbon particles react with the elements in the gold alloy to form the carbonaceous layer on the gold alloy. The carbonaceous composition in the metallic carbonaceous layer may include, but not limited to, carbides. Besides liberating free carbon particles, the intermediate zone also serves to reduce some of the metallic oxides inevitably formed during
15 the heating.

Oxides are inevitably formed on the surface of the gold alloy since there is a window period between the formation of the gold alloy and the heating step. Active elements such as titanium easily oxidize to form titanium oxides. The formation of oxides is even more prominent and severe during heating on a hot-
20 plate in open air or other similar oxidizing environments. To minimize the formation of oxides, it is therefore critical to coat a thin layer of oil on the gold alloy surface prior to the heating. The layer of oil will act as a diffusion barrier for atmospheric oxygen adsorbing onto the gold alloy surface and diffusing from the surface to the inner gold alloy, thereby preventing excessive oxidation. The thin
25 layer of oil also serves another advantage. By having the thin layer of oil over the gold alloy surface, an even heating can be achieved so that localized hot spots at different regions of the gold alloy are avoided.

There is yet another advantage afforded by the present invention. During the quenching of the gold alloy in the hydrocarbon medium, hydrocarbon molecules
30 immediately close to the gold alloy surface are subjected to high temperatures. Such high temperatures cause the neighbouring hydrocarbon molecules to

break down into carbon particles and hydrogen molecules. The carbon particles attach themselves to the surface of the gold alloy to further form the carbonaceous layer while the hydrogen molecules are liberated into the atmosphere.

- 5 The afore-described method provides a simple and economical way of producing blue, green or greenish-blue, maroon and black gold alloys using a single alloy composition. By heating the gold alloy to a selected temperature based on the desired colouring, coloured gold alloys are obtained. Conventional induction and electric arc furnaces are commercially available for melting and
10 forming different compositions gold alloys. Oxy-acetylene torches are also commercially available for carburizing the gold alloy. Low viscosity oils such as olive oil, organic oil and lubricating oil are cheaply available and can be reused and recycled. Scalability to production stage is also easily achieved since the method involves non-sophisticated equipments. Furthermore, about 10 – 20
15 grams of coloured gold alloy can be formed in relatively short time of less than one minute of heating at the selected temperature.

- The coloured gold alloy obtained via the afore-described method is subsequently light-polished to produce an intense, glossy coloured surface. The colouring formed on the gold alloy surface is physically and chemically stable for
20 daily use. The colouring does not deteriorate over time. This is due to the formation of a carbonaceous layer on the gold alloy surface. The carbonaceous layer has good interface adhesion with the underlying gold alloy. Furthermore, the dense carbonaceous layer provides a scratch-resistant layer protecting the underlying gold alloy, and provides sufficient corrosion resistance against body
25 acids for daily use, which makes the gold alloy suitable for use in jewellery and watch parts.

- Although the foregoing invention has been described in some detail by way of illustration and example, and with regard to one or more embodiments, for the purposes of clarity of understanding, it is readily apparent to those of ordinary
30 skill in the art in light of the teachings of this invention that certain changes,

variations and modifications may be made thereto without departing from the spirit or scope of the invention as described in the appended claims.

I CLAIM:

1. A method for forming coloured gold alloy, comprising the steps of:
 - coating a layer of oil on a gold alloy; and
 - heating the coated gold alloy at a temperature selected based on the
5 colouring on the gold alloy desired until the colouring appears;wherein the gold alloy comprises gold, titanium, and at least one other element.
2. The method recited in claim 1, wherein titanium content is more than 10 wt%.
- 10 3. The method recited in claim 2, wherein titanium content is 10 – 50 wt%.
4. The method recited in claim 1, 2, or 3, wherein gold content is 58 – 85 wt%.
5. The method recited in any one of the preceding claims, wherein the at least one other element is selected from the group consisting of:
 - 0 – 8 wt% Fe
 - 15 • 0 – 5 wt% Co
 - 0 – 5 wt% Cr
 - 0 – 5 wt% Mn
 - 0 – 5 wt% Mo
 - 0 – 5 wt% Pd
 - 20 • 0 – 5 wt% Nb
 - 0 – 5 wt% W
 - 0 – 6 wt% Al
 - 0 – 2 wt% Si.

6. The method recited in any one of the preceding claims, wherein the heating temperature is selected from the group consisting of:
- 400 – 500 °C for maroon coloured gold alloy;
 - 500 – 600 °C for blue coloured gold alloy;
 - 5 • 650 – 700 °C for green and greenish-blue coloured gold alloy; and
 - 800 – 900 °C for black coloured gold alloy.
7. The method recited in any one of the preceding claims, comprising heating the coated gold alloy in a carburizing environment.
8. The method recited in claim 7, comprising heating the coated gold alloy in
10 an oxy-acetylene environment.
9. The method recited in claim 8, comprising heating the coated gold alloy in an acetylene-rich oxy-acetylene environment.
10. The method recited in claim 8 or 9, wherein the volumetric flow rate of acetylene to oxygen in the oxy-acetylene environment is 5:3.
- 15 11. The method recited in any one of claims 1 – 6, comprising heating the coated gold alloy in air.
12. The method recited in claim 11, comprising heating the coated gold alloy on a hot-plate or furnace.
13. The method recited in any one of the preceding claims, wherein the oil
20 comprises low viscosity oil.
14. The method recited in claim 13, wherein the low viscosity oil is one of: olive oil; organic oil; lubricating oil.
15. The method recited in any one of the preceding claims, further comprising
25 cooling the heated gold alloy after the appearance of the colouring on the gold alloy.

16. The method recited in claim 15, comprising cooling the heated gold alloy to room temperature in still air.
17. The method recited in any one of claims 1 – 14, further comprising quenching the heated gold alloy in a quenching medium after the appearance of the colouring on the gold alloy.
18. The method recited in claim 17, wherein the quenching medium is a hydrocarbon.
19. The method recited in claim 18, wherein the quenching medium is low viscosity oil.
20. The method recited in claim 19, wherein the low viscosity oil is one of: olive oil; organic oil; lubricating oil.
21. The method recited in any one of claims 17 - 20, comprising quenching the heated gold alloy in the quenching medium at room temperature.
22. A coloured gold alloy comprising gold, titanium, and at least one other element formed according to any one of the preceding claims.
23. Jewellery comprising a coloured gold alloy comprising gold, titanium, and at least one other element formed according to any one of the preceding claims.
24. Use of a coloured gold alloy in jewellery, the coloured gold alloy comprising gold, titanium, and at least one other element formed according to any one of the preceding claims.