METHOD OF FORMING A METALLIC CARBIDE LAYER ON A GOLD ALLOY

FIELD OF INVENTION

The invention relates to a method of forming a metallic carbide layer on a gold alloy. In particular, the invention relates to the formation of a gold alloy having a black colouring by way of the metallic carbide layer.

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 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 increasingly high in demand compared to traditional yellowish gold. Black gold, in particular, is much sought after.

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

In a typical oxidation process, an alloy comprising gold and a colouring metallic element 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. The gold alloy obtained in this manner possesses a black-coloured surface due to the formation of a metallic oxide layer overlying the bulk of the gold alloy. Metallic oxide layers produced via the above-described oxidation process do not possess sufficient scratch resistance or durability for daily wear. Further, the layer of metallic oxide formed is often not dense enough to provide a deep dark colouration. On closer inspection of the metallic oxide layer, a dark blue non-uniform tint can be observed.

It is desirable to provide a deep dark colouration on a gold alloy that overcomes, or at least alleviates, the above problems. It is also desirable to provide a method of forming the deep dark colouration on a gold alloy, which method is simple and economical.

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 of forming a metallic carbide layer on a gold alloy comprising at least one other metallic element capable of forming the metallic carbide layer, the method comprising the steps of:

- heating the gold alloy in a non-oxidizing environment providing carbon precursors to react with the at least one other metallic element to form the metallic carbide layer; and
- quenching the gold alloy in a quenching medium containing further carbon precursors to further form the metallic carbide layer.

Preferably, the non-oxidizing environment is a carburizing environment. More preferably, the carburizing environment is an oxy-acetylene environment. Even more preferably, the oxy-acetylene environment is acetylene-rich.

Preferably, the step of heating the gold alloy involves heating the gold alloy at a temperature of between 600°C and 950°C, more preferably between 850°C and 950°C, and more preferably at 900°C.

Preferably, the step of quenching the gold alloy involves quenching the gold alloy in a hydrocarbon medium. The quenching medium is preferably low viscosity oil. More preferably, the low viscosity oil is one of: olive oil; organic oil; lubricating oil. Quenching is preferably conducted at room temperature.

Preferably, the at least one other metallic element in the gold alloy is selected from the following metals in their stated weight percentage ranges:

- 12 – 62.5 wt% Fe;
- 0 – 10 wt% Ti;
- 0 – 10 wt% Pd;
- 0 – 5 wt% Cr;
- 0 – 15 wt% Mn;
- 0 – 15 wt% Co;
- 0 – 5 wt% Mo;
- 0 – 62.5 wt% Nb; and
- 0 – 5 wt% W.

In a second aspect of the present invention, there is provided a gold alloy having a metallic carbide layer formed by the afore-described method.

DETAILED DESCRIPTION

The invention relates to a method of forming a metallic carbide layer on a gold alloy. In particular, the invention relates to the formation of a gold alloy having a black colouring by way of the metallic carbide layer.

In accordance with a first embodiment of the invention, there is provided a method of forming a metallic carbide layer on a gold alloy. The gold alloy preferably contains 37.5 - 75 weight percent (wt%) gold, otherwise commercially known as 9 - 18 carat gold. The balance of the gold alloy (i.e. 25 – 62.5 wt%) comprises at least one other metallic element that is capable of forming the metallic carbide layer on the gold alloy. Examples of the at least one other metallic element includes the following:

- 12 – 62.5 wt% Fe
- 0 – 10 wt% Ti
- 0 – 10 wt% Pd

- 0 – 5 wt% Cr
- 0 – 15 wt% Mn
- 0 – 15 wt% Co
- 0 – 5 wt% Mo
- 0 – 62.5 wt% Nb
- 0 – 5 wt% W

The gold alloy is heated in a non-oxidizing environment providing carbon precursors to react with the at least one other metallic element to form the metallic carbide layer.

In one embodiment, the gold alloy is heated using a carburizing flame. In a further embodiment, the carburizing flame consists of an oxy-acetylene flame. In yet another embodiment, the gold alloy is heated using an acetylene-rich oxy-acetylene flame. The carburizing flame is non-oxidizing. The carburizing 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.

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 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 structure of the gold alloy. Some of the carbon particles react with the at least one other metallic element to form the metallic carbide layer on the gold alloy. Besides liberating free carbon particles, the intermediate zone also serves to reduce some of the oxides formed during the heating.

The gold alloy is heated at temperatures suitable for the carbon to react with the at least one other metallic element to form the metallic carbide. In one embodiment, the gold alloy is heated at a temperature of between 600°C and 950°C. Preferably the temperature is between 850°C and 950°C, and more preferably at 900°C. Other heating temperatures are also suitable, depending on the types of metallic elements and their respective compositions in the gold alloy.

The heating of the gold alloy continues until a visible wetting appearance on the surface of the gold alloy is observed, otherwise known as the sweating phenomenon. This sweating phenomenon is due to the sudden increase in the carbon content on the surface of the gold alloy caused by the carburizing flame, which has the hot carbon particles in the intermediate zone. At this time, the gold alloy is cherry red in colour due to the sweating phenomenon.

Immediately after the sweating phenomenon occurs, the cherry red gold alloy is subsequently rapidly cooled or quenched in a quenching medium to further form a metallic carbide layer. The gold alloy is preferably quenched at room temperature. Other quenching temperatures to further form the metallic carbide layer are also suitable.

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.

During the quenching of the gold alloy in the hydrocarbon medium, hydrocarbon molecules immediately close to the cherry red 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 metallic carbide layer whilst the hydrogen molecules are liberated into the atmosphere.

Examples

Gold alloys are obtained 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 1 (18 carat

gold) illustrated in Table 1 below, 75 wt% Au, 20 wt% Fe, 3 wt% Mn, 1.5 wt% Cr, and 0.5 wt% Pd 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 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 for the formation of the metallic carbide layer.

Alloy 1 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 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. At this time, the sweating gold alloy is cherry red in colour.

The cherry red 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 cherry red 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 the metallic carbide layer. The olive oil bath container is exposed to air. Oxygen may be present at the olive oil surface. By having the cherry red 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.

Table 1 illustrates the exemplary compositions of 18 carat gold alloy suitable for the working of the invention.

Metal (wt%)	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5	Alloy 6	Alloy 7	Alloy 8	Alloy 9	Alloy 10
Fe	20	18	19	22	23	19	19	15	12	19
Co		2						3		
Cr	1.5		1	1	1	2	2	1	3	2
Mn	3	3	3	2		2	2	2	5	
Mo		1	1		1			2	3	
Pd	0.5	1	1				1		0.5	1
Ti							1	2	1.5	
Nb										3
W						2				

TABLE 1: Based on 999 Gold, 18 carat (75 wt% Au)

Table 2 illustrates the exemplary compositions of 14 carat gold alloy suitable for the working of the invention.

Metal (wt%)	Alloy 11	Alloy 12	Alloy 13	Alloy 14	Alloy 15	Alloy 16
Fe	30	35	33	20	26	23
Co			3	3	4	5
Cr	3	3			2	
Mn	8		3	3		3
Mo	0.5		2.5	2.5	2.5	2.5
Pd					0.5	6
Ti				10	5	2
Nb		2		1.5		
W		1.5		1.5	1.5	

TABLE 2: Based on 999 Gold, 14 carat (58.5 wt% Au)

Table 3 illustrates the exemplary compositions of 9 carat gold alloy suitable for the working of the invention.

Metal (wt%)	Alloy 17	Alloy 18	Alloy 19	Alloy 20
Fe	47	42	49	50
Co	5.5	4	7	5
Cr	0.5	3	3	4
Mn	3	8	0.5	2
Mo		0.5		
Pd	5	3	2	0.5
Ti	1	1	0.5	
Nb				0.5
W	0.5	1	0.5	0.5

TABLE 3: Based on 999 Gold, 9 carat (37.5 wt% Au)

The gold alloy having a metallic carbide layer thus obtained via the afore-described method is subsequently light-polished to produce an intense, glossy black surface. The metallic carbide layer has good interface adhesion with the underlying gold alloy. Furthermore, the dense metallic carbide layer provides a scratch-resistant layer protecting the underlying gold alloy, and provides sufficient corrosion resistance against body acids for daily use, which makes the gold alloy suitable for use in jewellery and watch parts.

The metallic carbide layer is physically and chemically stable for daily use. The black colouration it affords to the underlying gold alloy does not deteriorate over time.

The afore-described method provides a simple and economical way of producing black gold. Conventional induction and electric arc furnaces are commercially available for melting and forming different compositions gold alloys. Oxy-acetylene torches are also commercially available for carburizing the gold alloy. It takes approximately one minute for the sweating phenomenon at 900°C to occur. 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.

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 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 of forming a metallic carbide layer on a gold alloy comprising at least one other metallic element capable of forming the metallic carbide layer, the method comprising the steps of:

    - heating the gold alloy in a non-oxidizing environment providing carbon precursors to react with the at least one other metallic element to form the metallic carbide layer; and

    - quenching the gold alloy in a quenching medium containing further carbon precursors to further form the metallic carbide layer.

2. The method recited in claim 1, wherein the at least one other metallic element is selected from:

    - 12 – 62.5 wt% Fe;

    - 0 – 10 wt% Ti;

    - 0 – 10 wt% Pd;

    - 0 – 5 wt% Cr;

    - 0 – 15 wt% Mn;

    - 0 – 15 wt% Co;

    - 0 – 5 wt% Mo;

    - 0 – 62.5 wt% Nb;

    - 0 – 5 wt% W.

3. The method recited in claim 1 or 2, wherein the step of heating the gold alloy involves heating the gold alloy in a carburizing environment.

4. The method recited in claim 1, 2 or 3, wherein the step of heating the gold alloy involves heating the gold alloy in an oxy-acetylene environment.

5. The method recited in claim 4, wherein the oxy-acetylene environment is an acetylene-rich oxy-acetylene environment.

6. The method recited in claim 5, wherein the volumetric flow rate of acetylene to oxygen in the oxy-acetylene environment is 5:3.

7. The method recited in any preceding claim, wherein the step of heating the gold alloy involves heating the gold alloy at a temperature of between 600°C and 950°C.

8. The method recited in claim 7, wherein the step of heating the gold alloy involves heating the gold alloy at a temperature of between 850°C and 950°C.

9. The method recited in claim 8, wherein the step of heating the gold alloy involves heating the gold alloy at a temperature of 900°C.

10. The method recited in any preceding claim, wherein the step of quenching the gold alloy involves quenching the gold alloy in a hydrocarbon medium.

11. The method recited in claim 10, wherein the step of quenching the gold alloy involves quenching the gold alloy in a low viscosity oil.

12. The method recited in claim 11, wherein the low viscosity oil is one of: olive oil; organic oil; lubricating oil.

13. The method recited in any preceding claim, wherein the step of quenching the gold alloy involves quenching the gold alloy in the quenching medium at room temperature.

14. A gold alloy having a metallic carbide layer formed according to any one of the preceding claim.