TITLE:

AN ALLOY COMPOSITION FOR THE MANUFACTURE OF JEWELLERY

TECHNICAL FIELD

The present invention relates to jewellery alloy compositions.

BACKGROUND ART

Aluminium-gold alloys, with the comparable atomic size factors (2.878; 2.8577) and similar lattice crystal structures (f.c.c, face centred cubic) of their components and large variations in electronegativity factors, exist in a large diversity of microstructures and phases. The aluminium-gold phase diagram shows regions of solid solution, eutectic mixture and complex compounds such as $Au_5Al_3$, $AuAl_2$, gamma, etc. The $AuAl_2$ intermetallic compound is a complex cubic structure similar to ionic compounds and is a somewhat metastable form, with an electron to atom ratio of 3:2 and a weight percent ratio of 78.5% Au to 21.5% Al. This compound is of particular interest to jewellers and the like because of its brilliant purple-golden colour.

However, this interest is largely offset by the fact that the $AuAl_2$ intermetallic compound is extremely brittle. Like ordinary glass or porcelain, $AuAl_2$ will fracture with a hard knock. $AuAl_2$ is so brittle that it cannot be tested using the Rockwell B hardness testing machine with a 100 kg load, as it fractures even when around a 60 kg load is applied.

This problem of brittleness was addressed in Japanese patent application JP 61-30642 by lowering the gold component to 75% while employing aluminium in an amount of 20-24.5 wt% while at the same time introducing 0.5 to 5 wt% of one or two additional elements selected from silicon, magnesium, copper, zinc or manganese. By varying the relative amount of the additional element or elements, the tone or hue can be changed slightly while retaining the attractive purple colour.

However, as can be seen from the Au-Al phase diagram (Fig 1), lowering the gold content below 78.5 wt% in an AuAl system gives rise to the co-existence of two structures, $AuAl_2$ intermetallic compound and the eutectic structure of Al and $AuAl_2$ in the same sample.

Thus, upon slow cooling from the molten phase or upon annealing rapidly solidified samples, precipitation of the aluminium rich eutectic phase on the outward surface becomes evident and degrades the purple-golden colour. Even if rapidly solidified samples are not annealed, similar decolouration of the purple-gold colour may also occur after fabrication and polishing of the jewellery and possibly even through prolonged usage. Further, hardness of the eutectic and $AuAl_2$ phase is also significantly lower (around 10% for an alloy of 75 wt% gold and 25wt% aluminium) than that of the $AuAl_2$ intermetallic compound.

For these reasons, the viability of gold aluminium alloys where the gold content is less than 78.5 wt% is limited.

The present Applicant, in an earlier application (PCT/SG00/00013), showed that alloys of aluminium and gold provided purple compositions suitable for jewellery which comprised greater than 76 wt% gold. The hardness of these alloys could be further increased by the addition of alloying components such as nickel or palladium.

However, there is now effectively an international ban on the use of nickel in jewellery. It has been estimated that around 10% of women and 2% of men are allergic to nickel. A small minority of the population, estimated around 0.5%, experience a more severe reaction, including a rash on immediate contact with the metal. It is the object of the present invention to provide a jewellery alloy which overcomes the above stated disadvantages or at least provides a commercial alternative.

"Jewellery alloy" as herein defined is an alloy having sufficient toughness to withstand Rockwell B hardness testing with a 100 kg load without shattering. Being able to use Rockwell B hardness testing is perceived as an empirical measure that the alloy is suitable for fabricating jewellery. If the alloy is too brittle to withstand Rockwell B hardness testing, then it is too brittle to be used in jewellery.

Further, those skilled in the art will appreciate that alloys able to withstand Rockwell testing to a higher standard, especially in particular Rockwell C hardness testing, will be even more suitable for jewellery than materials which can only withstand Rockwell B hardness testing.

In addition, it has been observed by the present inventor that in some cases where the purple gold is being cast into particularly small, fine or intricate articles, defects such as fine cracks (micro-fissuring), regions of porosity and yellowish patches become evident.

One reason why this phenomenon may be more prevalent in small, fine or intricate castings is because the casting temperatures under those circumstances are required to be increased in order to allow for the molten liquid purple gold to be more fluid and enter the fine cavities completely. It is known to those skilled in the art that the use of higher casting temperatures slows down the overall solidification process and results in greater shrinkage and stress.

It is an object of the present invention to overcome or ameliorate at least one of the abovementioned disadvantages of the prior art, or to provide a useful alternative.

The term "jewellery" is intended to cover ornamental objects for personal adornment or otherwise, including medallions, coins and the like where the stated toughness is a prerequisite.

DESCRIPTION OF THE INVENTION

According to a first aspect the invention provides a nickel-free jewellery alloy as herein defined including:

78.5-83 wt% gold;

17-20.5 wt% aluminium;

a nickel-free alloying component; and

wherein said alloy has a substantially purple hue.

Preferably the nickel-free alloying component is present in an amount of not more than 2 wt%. In highly preferred embodiments, the nickel-free alloying component is α-manganese.

In certain preferred embodiments, the nickel-free jewellery alloys of the present invention have a Rockwell C hardness (HRC) of at least 16.5.

In the nickel-free jewellery alloy of the present invention, the nickel-free alloying component preferably includes α-manganese and one or more components selected from the group consisting of magnesium, zinc, copper, indium, silicon, iron, hafnium, vanadium and palladium.

Preferably, the alloying component includes α-manganese and palladium.

More preferably, the alloying component includes α-manganese, copper and palladium.

More preferably, the alloying component includes α-manganese, copper, palladium and magnesium. In an alternative preferred embodiment, the alloying component includes α-manganese, copper, palladium and iron. In a further alternative preferred embodiment, the alloying component includes α-manganese, copper, palladium and silicon.

It is also preferred if the alloying component further includes one or more of indium, hafnium or vanadium.

It is preferred that α-manganese is present in an amount of 0.1 to 0.5 wt% of the alloy, and more preferably 0.25 to 0.4% of the alloy.

It is preferred that, where present, copper is present in an amount of 0.1 to 0.3 wt% of the alloy, and more preferably 0.2 to 0.3% of the alloy. Brass may also be used in similar quantities.

It is preferred that, where present, palladium is present in an amount of 0.05 to 0.6 wt% of the alloy, and more preferably 0.25 to 0.4% of the alloy.

It is preferred that, where present, magnesium is present in an amount of 0.001 to 0.05 wt% of the alloy, and more preferably 0.01 to 0.02% of the alloy.

It is preferred that, where present, iron is present in an amount of 0.001 to 0.05 wt% of the alloy.

It is preferred that, where present, silicon is present in an amount of 0.01 to 1.6%. If the silicon is added to prevent micro-fissuring and the like in small castings, it is preferably present in an amount of 1 to 1.6wt% of the alloy and palladium, manganese and other additives may be absent. Alternatively, silicon may be present in an amount of 0.01 to 0.06 wt% of the alloy, and more preferably 0.02 to 0.04% of the alloy.

It is preferred that, where present, indium is present in an amount of 0.05 to 0.2 wt% of the alloy, and more preferably around 0.15% of the alloy.

It is preferred that, where present, vanadium is present in an amount of 0.2 to 0.4 wt% of the alloy, and more preferably around 0.3% of the alloy.

It is preferred that, where present, hafnium is present in an amount of 0.05 to 0.2 wt% of the alloy, and more preferably around 0.1% of the alloy.

In a second aspect, the invention provides an article including a metal component, the metal component including a jewellery alloy according to the first aspect.

Preferably, the article is selected from the group consisting of ornamental jewellery, medallions and coins.

According to a third aspect, the invention provides an alloying compound for inclusion into a gold-aluminium alloy, said alloying compound including α-manganese, and palladium. Preferably, the alloying compound also includes copper.

More preferably, the alloying compound further includes one or more metals selected from the group consisting of magnesium, indium, silicon, iron, hafnium and vanadium.

According to a fourth aspect, the invention provides a method of improving the mechanical properties of an alloy including the step of adding to the alloy an alloying compound according to the third aspect. Preferably, the alloying compound is added in an amount up to 2 wt% of the alloy.

According to a fifth aspect, the invention provides the use of an alloying compound of the third aspect for the preparation of a nickel-free jewellery alloy.

According to a sixth aspect the invention provides a nickel-free jewellery alloy as herein defined including:

78.5-83 wt% gold;

17-20.5 wt% aluminium;

1-1.6 wt% silicon

a nickel-free alloying component; and

wherein said alloy has a substantially purple hue.

By definition, the jewellery alloy of the present invention excludes pure intermetallic gold compound $AuAl_2$ which has 78.5 wt% gold and 21.5 wt% aluminium because it does not have the requisite toughness to withstand Rockwell B hardness testing with the 100 kg load, and because the alloying component is absent.

The term "substantially purple hue" as herein used includes the colours reddish or pinkish-purple and lighter purples. Those skilled in the art will be familiar with the particular ranges achievable which are comparable to those achievable in the traditional brittle purple gold alloys.

The term "nickel free" refers to any alloy containing no nickel detectable by any means, as well as encompassing those compositions where nickel is present in trace amounts which may be detectable by instrumental analysis but have no recognised physiological effect on a wearer. The term "nickel free" may also be quantified as being below the lower limit set by regulatory authorities, for example the EC regulations which specify les than 0.05% total nickel with a release of less than $0.5\mu g/cm^2$/week.

Preferably, the hardness of the jewellery alloy of the present invention remains substantially similar, or at least no weaker to, that of the $AuAl_2$ intermetallic compound. That is, the hardness of the alloy is at least 94%, and most preferably 95% or greater of the hardness of $AuAl_2$.

Turning to the issue of micro-fissuring, porosity and formation of yellowish patches, without wishing to be bound by theory, these defects are believed by the present inventor to be a result of localised segregation of a Si-Al compound along the purple gold grain-boundaries replacing the gamma-Au-Al compound.

The region of segregation was found to contain a Si-Al compound containing 0.5-1.0 wt% silicon. This is not withstanding that the present overall content of silicon in the purple gold is typically less than 0.01 wt%. Thus, casting at higher temperatures can result in up to a one hundred-fold localised enhancement of silicon which can cause micro-fissuring and other defects.

By analogy, it is known that in Al-Si alloys, if the silicon is present in an amount between 0.5-1 wt% and allowed to cool slowly, many fine cracks will occur. The critical

temperature range at which cracking occurs is 600°C-570°C which is known as the nil ductility temperature range.

Surprisingly, the present inventor has found that by increasing the overall silicon content of the alloy, in some cases up to 1-1.6 wt%, either with or without the addition of palladium and/or manganese and others elements, the cracking or micro-fissuring disappeared or was substantially reduced. The reason for this would appear to be that at higher silicon content, there is a higher chance of forming a better ductility Au-Si compound (which forms at 363°C) which displaces the lower ductility Si-Al compound. It was also found that some boundary regions contain a higher Si-Al compound of more than 10% Si by weight. These higher Si-Al compounds seem to be beneficial as well.

Without wishing to be bound by theory, it could be that at this composition range of the Paste Region in the Al-Si phase diagram (otherwise known as the solidus-liquidus gap) becomes very narrow, hence escaping the weakness of the large Paste Region. Solidus is the temperature at which an alloy starts to melt, liquidus is the temperature at which an alloy is completely molten, with no solid phase regions remaining. It was further realised that at higher silicon content, the many micro particles of Silicate in the liquid would help to promote nucleation at multiple sites resulting in finer grains with a tougher structured purple gold without any effect to the purple colour hue. Further, the higher silicon content also helps to lower the purple gold melting point, increasing the fluidity.

Thus, by adding additional amounts of silicon, casting can be done at lower temperature with lower shrinkages, lower stresses and porosity. In conclusion, the use of a higher silicon alloy with or without palladium was found to address the problems of micro-fissuring porosity in fine, small or intricate purple gold jewellery castings.

A better understanding of the present invention may be obtained in light of the following examples embodying the invention which is set forth to illustrate, in a non-limiting way, the present invention.

α-Manganese is known to those skilled in the art to be a Mn/Co solid solution, with a maximum of 10% Cobalt, the remainder being manganese.

BEST MODE FOR CARRYING OUT THE INVENTION

Eight examples of alloys embodying the present invention and 2 comparative alloys were manufactured and tested as follows:

1) Where stated, specimens were tested using a Rockwell C hardness testing machine with a 150 kg load. For those specimens which would not withstand Rockwell C hardness testing, Rockwell B hardness testing, using a 100 kg load, was employed.

All specimens were annealed at 600°C and examined for precipitation of low melting point aluminium-rich eutectic material. The presence of such precipitation would be evident from the appearance of a greyish-white colour between reddish purple regions on the specimens surface.

Any conventional annealing process which allows annealing at 600°C is suitable for carrying out the present invention. Annealing at 600°C avoids precipitation of Al-rich eutectic and γ-phase mixtures.

Control 1 (78.5 wt% Au and 21.5 wt% Al)

The $AuAl_2$ intermetallic compound had a brilliant purple hue but was known to be brittle. Micro-hardness testing with a 200g load gave a reading of Vickers 250. A Vickers 250 hardness translates to a Rockwell hardness (HRB) of 102. Subsequent testing with Rockwell B hardness machine resulted in multiple fracturing of the specimen.

After annealing of the sample, no visible precipitates were found.

Control 2 (75 wt% Au and 25 wt% Al)

The specimen had a reddish-purple colour but was softer and less brittle than Control 1, having a Rockwell B hardness of 91.

Annealing of the material showed large amounts of aluminium rich eutectic precipitation seriously degrading the surface reddish-purple colour of the material.

Example 1

Gold 80.2%, aluminium 18.84%, α-manganese 0.25%, copper 0.25%, palladium 0.4%, magnesium 0.02%, iron 0.005%.

The average Rockwell C hardness (HRC) was found to be 20 and the tough material showed no precipitation after annealing at 600°C. The colour was of a good purplish tone with a bluish-reddish hue.

Example 2

Gold 80.15%, aluminium 18.99%, copper 0.1%, α-manganese 0.1%, palladium 0.6%, magnesium 0.05%, iron 0.005%.

The average hardness was found to be 21.6 Rockwell C and the tough material showed no precipitation of a eutectic phase upon heating at 600°C. The colour showed a rich purplish tone with a reddish hue.

Example 3

Gold 80.1% aluminium, 18.69%, α-manganese 0.4%, copper 0.2%, palladium 0.6%, magnesium 0.001%, iron 0.001%.

The average hardness was 21.5 HRC. No precipitation was observed on heating to 600°C. The colour showed a good purplish tone with a bluish hue.

Example 4

Gold 80.3%, aluminium 18.97%, α-manganese 0.4%, brass 0.27%, silicon ≤ 0.01%, palladium 0.05%.

Rockwell hardness was 16.5 HRC with no precipitation upon annealing at 600°C. The material had good fluidity during casting and the colour of the material was a good purplish tone with a reddish hue.

Example 5

Au 80.15%, Al 18.79%, α-manganese 0.5%, palladium 0.4%, indium 0.05%, magnesium 0.001% and iron 0.109%.

The average hardness of the mixture was 20 HRC with no precipitation upon annealing at 600°C. The colour was a beautiful purplish tone with a bluish hue.

Example 6

Au 80.3%, Al 18.9%, α-manganese 0.25%, copper 0.25%, palladium 0.25%, silicon 0.04%, magnesium 0.001%, iron 0.001%.

The average hardness was 18.3 HRC. There was no precipitation observed upon annealing to 600°C. The colour was a good purplish-reddish tone.

Example 7

Gold 80.15%, aluminium 18.76%, hafnium 0.1%, copper 0.2%, α-manganese 0.3%, palladium 0.4%, silicon 0.06%.

The average hardness was 19.6 HRC with no precipitation upon heating to 600°C. The colour was purplish-reddish light blue.

Example 8

Gold 80.18%, aluminium 18.56%, vanadium 0.3%, α-manganese 0.3%, copper 0.2%, vanadium 0.4% and silicon 0.06%.

The average hardness was 20.6 HRC. No precipitation was observed upon annealing to 600°C. The colour was purplish-reddish blue.

Example 9

Gold 80%, aluminium18.5%, silicon 1.38 wt% with traces of manganese, magnesium and iron of not more than 0.12 wt%.

The average hardness was 28.5 HRC with no precipitation upon annealing at 600°C. The colour was a rich bluish-red-purple hue.

Example 10

Gold 80 wt%, aluminium18.5%, silicon 1.0 wt%, palladium 0.38 wt% and with traces of manganese, magnesium and iron of not greater than 0.12 wt%.

The average hardness was 27 HRC with no precipitation upon annealing at 600°C. The colour was rich bluish-red-purple hue.

The foregoing examples were testing with a severe loading of 150 kg with a sharp pointed diamond indenter (HRC). All the examples of the present application were found to be ductile and tough without fracture. The temperature of 600°C was selected for because this was above that which can be withstood by the gamma phase of the AuAl phase diagram. Thus, any heating above this temperature would reveal precipitation of Al-rich eutectic and γ-phase mixtures.

The field tests of the gold alloys of the present invention show good colour stability over time and also a good degree of resistively when exposed to fatty or uric acids.

It will be clear to those skilled in the art that the present invention may be practised in a manner other than that particularly described in the foregoing description and non-limiting examples.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A nickel-free jewellery alloy as herein defined including:

78.5-83 wt% gold;

17-20.5 wt% aluminium;

a nickel-free alloying component; and

wherein said alloy has a substantially purple hue.

2. A nickel-free jewellery alloy according to claim 1 wherein the nickel-free alloying component is present in an amount of not more than 2 wt%.

3. A nickel-free jewellery alloy according to claim 1 or claim 2 wherein the nickel-free jewellery alloy includes α-manganese.

4. A nickel-free jewellery alloy according to any one of the preceding claims wherein the nickel-free alloying component includes α-manganese and one or more components selected from the group consisting of magnesium, brass, copper, indium, silicon, iron, hafnium, vanadium and palladium.

5. A nickel-free jewellery alloy according to any one of the preceding claims having a Rockwell C hardness of at least 16.5.

6. A nickel-free jewellery alloy according to any one of the preceding claims wherein the alloying component includes α-manganese and palladium.

7. A nickel-free jewellery alloy according to claim 6 wherein the alloying component includes α-manganese, copper and palladium.

8. A nickel-free jewellery alloy according to claim 6 wherein the alloying component includes α-manganese, copper, palladium and magnesium.

9. A nickel-free jewellery alloy according to claim 6 wherein the alloying component includes α-manganese, copper, palladium and iron.

10. A nickel-free jewellery alloy according to claim 6 wherein the alloying component includes β-manganese, copper, palladium and silicon.

11. A nickel-free jewellery alloy according to any one of claims 6 to 10 wherein the alloying component further includes indium.

12. A nickel-free jewellery alloy according to any one of claims 6 to 11 wherein the alloying component further includes hafnium.

13. A nickel-free jewellery alloy according to any one of claims 6 to 12 wherein the alloying component further includes vanadium

14. A nickel-free jewellery alloy according to any one of the preceding claims wherein α-manganese is present in an amount of 0.1 to 0.5 wt% of the alloy.

15. A nickel-free jewellery alloy according to claim 14 wherein α-manganese is present in an amount of 0.25 to 0.4% of the alloy.

16. A nickel-free jewellery alloy according to any one of the preceding claims wherein copper is present in an amount of 0.1 to 0.25 wt% of the alloy.

17. A nickel-free jewellery alloy according to claim 16 wherein copper is present in an amount of 0.2 to 0.3 wt% of the alloy.

18. A nickel-free jewellery alloy according to any one of the preceding claims wherein palladium is present in an amount of 0.05 to 0.6 wt% of the alloy.

19. A nickel-free jewellery alloy according to claim 18 wherein palladium is present in an amount of 0.25 to 0.4% of the alloy.

20. A nickel-free jewellery alloy according to any one of the preceding claims wherein magnesium is present in an amount of 0.001 to 0.05 wt% of the alloy.

21. A nickel-free jewellery alloy according to claim 20 wherein magnesium is present in an amount of 0.01 to 0.02% of the alloy.

22. A nickel-free jewellery alloy according to any one of the preceding claims wherein iron is present in an amount of 0.001 to 0.005 wt% of the alloy.

23. A nickel-free jewellery alloy according to claim 22 wherein iron is present in an amount of around 0.003 wt% of the alloy.

24. A nickel-free jewellery alloy according to any one of the preceding claims wherein silicon is present in an amount of 0.01 to 1.6 wt% of the alloy.

25. A nickel-free jewellery alloy according to any one of the preceding claims wherein silicon is present in an amount of 0.01 to 0.06 wt% of the alloy.

26. A nickel-free jewellery alloy according to claim 25 wherein silicon is present in an amount of 0.02 to 0.04% of the alloy.

27. A nickel-free jewellery alloy according to any one of claims 1-24 wherein silicon is present in an amount of 1 to 1.6 wt% of the alloy.

28. A nickel-free jewellery alloy according to any one of the preceding claims wherein indium is present in an amount of 0.05 to 0.2 wt% of the alloy.

29. A nickel-free jewellery alloy according to claim 28 wherein indium is present in an amount of around 0.15% of the alloy.

30 A nickel-free jewellery alloy according to any one of the preceding claims wherein vanadium is present in an amount of 0.2 to 0.4 wt% of the alloy.

31. A nickel-free jewellery alloy according to claim 30 wherein vanadium is present in an amount of around 0.3% of the alloy.

32. A nickel-free jewellery alloy according to any one of the preceding claims wherein hafnium is present in an amount of 0.05 to 0.20 wt% of the alloy.

33. A nickel-free jewellery alloy according to claim 32 wherein hafnium is present in an amount of around 0.1% of the alloy.

34. An article including a metal component, the metal component including a jewellery alloy according to any one of the preceding claims.

35. An article according to claim 34, wherein the article is selected from the group consisting of ornamental jewellery, medallions and coins.

36. An alloying compound for inclusion into a gold-aluminium alloy, said alloying compound including α-manganese.

37. An alloying compound according to claim 36 further including one or more metals selected from the group consisting of palladium, copper, brass, magnesium, indium, silicon, iron, hafnium and vanadium.

38. A method of improving the mechanical properties of an alloy including the step of adding an alloying compound according to claim 36 or 37.

39. A method of improving the mechanical properties of an alloy according to claim 38 wherein the alloying compound is added in an amount up to 2 wt% of the alloy.

40. The use of an alloying compound according to claim 36 or 37 for the preparation of a nickel-free jewellery alloy.

41. A nickel free jewellery alloy substantially as herein described with reference to any one of the examples, but excluding the comparative examples.

42. A nickel-free jewellery alloy as herein defined including:

78.5-83 wt% gold;

17-20.5 wt% aluminium;

1-1.6 wt% silicon;

a nickel-free alloying component; and

wherein said alloy has a substantially purple hue.

43. A nickel-free jewellery alloy according to claim 42 wherein the alloying component contains manganese, magnesium, iron or mixtures thereof in an amount of less then 0.12%.

44. A nickel-free jewellery alloy according to claim 43 further including Palladium.

45. A nickel free jewellery alloy according to any one of claims 42 to 44 wherein the amount of silicon plus Palladium is between 1 and 1.5%.

46. A nickel free jewellery alloy according to any one of claims 42 to 44 wherein the amount of silicon plus Palladium is about 1.38 %.