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(54) **METAL ALLOY COMPRISING GOLD**

(57) The present invention concerns a metal alloy comprising at least four metallic elements different from gold (Au), each of said metallic elements being in an amount from 1.0 to 55.0 atomic percent, characterized in that the metal alloy further comprises gold (Au) in an amount of at least 58.3 % by weight over the total weight of the metal alloy.

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Description

[0001] The present invention relates to a metal alloy comprising several metallic elements including gold (Au), and a process of manufacturing said metal alloy.

[0002] More particularly, the metal alloy is used to manufacture luxury goods.

[0003] It exists several types of metal alloys used to manufacture luxury goods such as a time-piece or a jewel. One can cite the document WO 2019/073023 concerning a metal alloy comprising at least four metallic elements such as scandium (Sc), aluminum (Al), titanium (Ti) and lithium (Li).

[0004] However, despite the various metal alloys which are commercially available, there is still a need to have new alternative metal alloys able to be used in the domain of luxury goods, with optimized properties.

[0005] In this respect, the present invention seeks to provide a new metal alloy, having optimized mechanical properties, while being easy to shape.

[0006] To this end, an object of the present invention is a metal alloy comprising at least four metallic elements different from gold (Au), each of said metallic elements being in an amount from 1.0 to 55.0 atomic percent (at%), characterized in that the metal alloy further comprises gold (Au) in an amount of at least 58.3% by weight over the total weight of the metal alloy.

[0007] The present invention advantageously provides a metal alloy with an improved hardness, while guaranteeing a good ductility. More particularly, the hardness of the metal alloy can advantageously be of at least 150 Vickers hardness (HV) (i.e. kilograms-force per square millimeter), more preferably of at least 200 HV, and even more preferably of at least 250 HV.

[0008] The metal alloy is also advantageously easy to shape, especially to manufacture luxury good.

[0009] The metal alloy of the present invention has advantageously a high entropy.

[0010] More particularly, the entropy of the metal alloy can be of at least 0.69R, more preferably at least 1.00R, and even more preferably at least 1.20R, R being the molar gas constant.

[0011] The entropy can be easily determined by the man skilled in the art, according to the well-known Boltzmann's definition related to the following equation: $\Delta S_{conf} = - R\Sigma X_i ln(X_i)$, where X_i represents the atomic fraction of element i and R is the molar gas constant.

[0012] A high entropy can favor the formation of a solid solution, which may help to improve the ductility of the metal alloy.

[0013] The metal alloy of the present invention can be a solid solution. A solid solution is well known in the art and can be considered as a solid-state solution comprising several metallic elements wherein the metallic elements remain in a single homogeneous phase in the metal alloy. Thus, the metal alloy of the invention can preferably be a single-phase alloy.

[0014] In the present invention, gold (Au) is used as main metallic element among the at least five metallic elements constituting the metal alloy.

[0015] Indeed, among the at least five metallic elements, the metal alloy comprises an amount of gold (Au) superior or equal to 58.3 % by weight over the total weight of the metal alloy.

[0016] An amount of gold (Au) of at least 58.3 % by weight over the total weight of the metal alloy is particularly advantageous since it corresponds to an amount of 583 ‰ (per mille) by weight of gold (Au) over the total weight of the metal alloy. With this lower limit of at least 583 ‰ by weight of gold (Au), the metal alloy can be considered as a precious material of 14-karat gold (i.e. 14k), under the karat standard system for gold alloy.

[0017] In a particular embodiment, the metal alloy can comprise at least 70.0 % by weight of gold (Au), and more preferably 75.0 % by weight of gold (Au), over the total weight of the metal alloy.

[0018] An amount of gold (Au) of at least 75.0 % by weight over the total weight of the metal alloy is particularly advantageous since it corresponds to an amount of 750 ‰ (per mille) by weight of gold (Au) over the total weight of the metal alloy. With this lower limit of at least 750 ‰ by weight of gold (Au), the metal alloy can be considered as a precious material of 18-karat gold (i.e. 18k), under the karat standard system for gold alloy.

[0019] In the present invention, the metal alloy comprises at least four metallic elements different from gold (Au), each of said four metallic elements being in an amount from 1.0 to 55.0 atomic percent (at%), and more preferably from 5.0 to 30.0 atomic percent.

[0020] The atomic percent of each metallic elements constituting the metal alloy is expressed over the total atomic percent (100%) of the metallic elements constituting the metal alloy.

[0021] The four metallic elements can be selected among silver (Ag), aluminum (Al), manganese (Mn), copper (Cu), palladium (Pd), iron (Fe), and chromium (Cr), platinum (Pt), and cobalt (Co).

[0022] In a first embodiment, the four metallic elements can be copper (Cu), silver (Ag), manganese (Mn), and aluminum (Al).

[0023] According to this first embodiment, the metal alloy can be for example, in at%, $Au_{34.4}Cu_{25.9}Ag_{22.8}Mn_{9.6}Al_{7.3}$ or $Au_{52.5}Cu_{20.3}Ag_{15.2}Mn_{6.5}Al_{5.5}$.

[0024] In a second embodiment, the four metallic elements can be palladium (Pd), silver (Ag), chromium (Cr), and iron (Fe).

[0025] According to this second embodiment, the metal alloy can be for example, in at%, $Au_{36.6}Pd_{16.4}Ag_{16.2}Cr_{15.4}Fe_{15.4}$.

[0026] In a third embodiment, the four metallic elements can be silver (Ag), chromium (Cr), palladium (Pd), and cobalt (Co).

[0027] According to this third embodiment, the metal alloy can be for example, in at%, $Au_{38.0}Ag_{15.5}Cr_{15.5}Pd_{15.5}Co_{15.5}$.

[0028] In a fourth embodiment, the four metallic elements can be silver (Ag), cobalt (Co), palladium (Pd), and iron (Fe).

[0029] According to this fourth embodiment, the metal alloy can be for example, in at%, $Au_{38.0}Ag_{15.5}Co_{15.5}Pd_{15.5}Fe_{15.5}$.

[0030] In a fifth embodiment, the four metallic elements can be silver (Ag), platinum (Pt), palladium (Pd), and iron (Fe).

[0031] According to this fifth embodiment, the metal alloy can be for example, in at%, $Au_{67.0}Ag_{8.25}Pt_{8.25}Pd_{8.25}Fe_{8.25}$.

[0032] The gold (Au) used in the metal alloy of the invention can preferably have a purity of at least 99.5 %, and more preferably of at least 99.9 % and even more preferably of at least 99.99 %.

[0033] The metallic elements different from gold (Au) can also have a purity of at least 99.0 %, and more preferably of at least 99.9 %.

[0034] Another object of the present invention is a process of manufacturing said metal alloy, the process comprising the following steps:

i. forming a molten alloy comprising gold (Au) and the at least four metallic elements different from gold,
ii. cold rolling the alloy obtained in step i, and
iii. optionally, annealing the alloy obtained in step ii.

[0035] The step i can include a mixture of the metallic elements as such and/or one or several pre-alloy(s).

[0036] The step i can be done in using an arc furnace, classically in placing the metallic elements and/or the pre-alloy(s) in a crucible, and submitting then with an electric arc producing a temperature of up to 3000°C. This process makes it possible to produce alloys from pure elements with different melting temperatures. The metallic element mixture can then be cooled to room temperature (around 25°C).

[0037] In another embodiment, the step i can be done in using an induction furnace, classically in placing the metallic elements and/or the pre-alloy(s) in a crucible, and submitting then with an induction heating. The metallic element mixture can then be cooled to room temperature (around 25°C).

[0038] A pre-alloy can be a mixture of at least two metallic elements having similar melting temperature. For example, a pre-alloy can be formed with two metallic elements having a melting temperature difference inferior or equal to 150°C, and more preferable inferior or equal to 100°C.

[0039] The pre-alloys can be formed in using an arc furnace. The metallic element mixture can then be cooled to room temperature (around 25°C).

[0040] The alloy obtained in step i is then rolled in order to increase its mechanical properties and modify its internal structure. The rolling step can be done at room temperature (around 25°C) in using a rolling mill. The rolling step can usually be performed after cooling to room temperature (around 25°C) the alloy obtained in step i.

[0041] The step iii can be advantageously done to improve the yield strength and the hardness of the alloy, especially when several cold rolling passes are done.

[0042] The temperature and annealing time depend on the nature of the alloy, the rate of cold work previously applied and the properties required, according to the conditions well-known in the art.

[0043] For example, the annealing step can be done at a temperature around 750°C, during 30 minutes.

[0044] In a particular embodiment, when the step iii is performed, the step iii can be followed by one or several steps of cold rolling as detailed in step ii.

[0045] Another object of the present invention is an item obtained from the metal alloy.

[0046] The item can comprise or consist of the metal alloy according to the present invention. Accordingly, the metal alloy can be used in order to manufacture luxury goods, such as for example a time-piece and/or a jewel. The time-piece and/or the jewel can have a part or a component comprising the metal alloy according to the present invention.

[0047] More particularly, the item according to the present invention can be a jewel, a leather good, or a clothing accessory. It may also be a watch, a writing accessory, or a decorative item.

[0048] For instance, the item can be any of the followings: ring; ear ring; necklace; bracelet; pendant; watch such as case, bezel, caseback, crown, bracelet links, clasp, buckle, automatic movement rotor; buckle (e.g. belt or purse); tie bar; cuff links; money clip; hair pin; pen; paper knife.

[0049] The present invention will become more fully understood from the examples given herein below, which are given by way of illustration only, and thus, which are not limits of the present invention.

Examples:

1. Preparation of the metal alloys according to the invention

[0050] Different metal alloys according to the present invention, i.e. Metal alloy 1, Metal alloy 2, Metal alloy 3, Metal alloy 4 and Metal alloy 5, have been prepared and are respectfully gathered in the following Tables 1 to 5.

[0051] The amounts in Tables 1 to 5 are expressed:

- in atomic percent (at%) over all the metallic element constituting the metal alloy, and
- in weight percent (wt%) over the total weight of the metal alloy.

[0052] According to the amount of gold, Metal alloy 1, Metal alloy 3 and Metal alloy 4 can be considered as a precious alloy of 14-karat gold, and Metal alloy 2 and Metal alloy 5 can be considered as a precious alloy of 18-karat gold.

Table 1

Metal alloy 1	Au	Cu	Ag	Mn	Al	Total
Atomic percent (at%)	34.4	25.9	22.8	9.6	7.3	100
Weight percent (wt%)	58.4	14.2	21.2	4.5	1.7	100

Table 2

Metal alloy 2	Au	Cu	Ag	Mn	Al	Total
Atomic percent (at%)	52.5	20.3	15.2	6.5	5.5	100
Weight percent (wt%)	75.1	9.3	12.0	2.6	1.0	100

Table 3

Metal alloy 3	Au	Pd	Ag	Cr	Fe	Total
Atomic percent (at%)	36.6	16.4	16.2	15.4	15.4	100
Weight percent (wt%)	58.3	14.1	14.1	6.5	7.0	100

Table 4

Metal alloy 4	Au	Ag	Cr	Pd	Co	Total
Atomic percent (at%)	38.0	15.5	15.5	15.5	15.5	100
Weight percent (wt%)	59.8	13.3	6.4	13.2	7.3	100

Table 5

Metal alloy 5	Au	Ag	Pt	Pd	Fe	Total
Atomic percent (at%)	67.0	8.25	8.25	8.25	8.25	100
Weight percent (wt%)	77.47	5.22	9.45	5.15	2.71	100

[0053] The preparation of the metal alloys gathered in Tables 1-5 is described as follows.

[0054] Firstly, a molten alloy is formed (step i) in using an arc furnace, in placing and mixing all the metallic elements constituting a metal alloy, in a crucible.

[0055] After cooling to room temperature (around 25°C) the alloy obtained in step i, a rolling step is performed (step ii) at room temperature (around 25°C), with several passes, in using a roller mill.

[0056] The rolling step is of:

- 83% to obtain the Metal alloy 1,
- 90% to obtain the Metal alloy 2,
- 70% to obtain the Metal alloy 3,
- 70% to obtain the Metal alloy 4,
- 60% to obtain the Metal alloy 5,

[0057] The rolled alloy is under the form of a bar.

2. Characterization of the metal alloys

[0058] Some properties of the metal alloys obtained in the preparation as described above can be easily determined, such as entropy, ΔE and hardness.

2.1. Determination of the entropy

[0059] The entropy is determined following the equation ΔS_{conf}= - $R\Sigma X_i ln(X_i)$, where X_i represents the atomic fraction of element i and R is the molar gas constant.

2.2. Determination method of the color

[0060] In order to evaluate the color of a metal alloy, the CIELAB coordinates, which are well known as color space specified by the International Commission on Illumination (known in French with the acronym CIE), are used.

[0061] The three coordinates of CIELAB represent the lightness of the color (L* = 0 yields black and L* = 100 indicates diffuse white), its position between red/magenta and green (a*, negative values indicate green while positive values indicate magenta) and its position between yellow and blue (b*, negative values indicate blue and positive values indicate yellow).

[0062] To compare two different colors, or to characterize the evolution of a sample, the expression "ΔE*" can be used. ΔE* corresponds to the distance between two colors placed in the CIELAB color space which is calculated with the formula of the Euclidian distance. ΔE* can also be written ΔE or ΔE_{ab}.

[0063] ΔE* is classically known as follows:

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

wherein: L_1^* , a_1^* , b_1^* are the coordinates of the first color to compare, and L_2^*, a_2^*, b_2^* are the coordinates of the second color to compare.

[0064] The illuminant used to evaluate the metal alloy color is the CIE D65 standard illuminant, with a viewing angle of 10°.

[0065] The evolution of the metal alloy color is studied according to the test Tuccillo-Nielsen wheel method, which aims at evaluating the tarnish testing of an alloy in contact with the skin. In this respect, the metal alloy is immersed during 30 seconds in artificial sweet and then dried in the open air during 30 seconds, in a continuous way. The artificial sweet composition used for the test is the composition according to European Committee for Standardization EN 1811, which is a solution of 0.5% NaCl, 0.1% urea and 0.1% lactic acid, with a pH adjusted to 6.5 using NH_4OH. Color measurements are taken at t=0, 4, 7, 15 and 25 days.

[0066] Finally, ΔE between t=0 and t=25 days is calculated. Hence, a low ΔE means a low color evolution.

2.3. Determination method of the hardness

[0067] In order to evaluate the hardness of a metal alloy, a Vickers micro-hardness tester on polished samples has been used. The samples have been indented linearly on the surfaces at five different positions and the average have been recorded. The indentation load was 2 kg with an indentation time of 10 seconds.

[0068] In the present invention, the hardness of the metal alloy can advantageously be of at least 200 HV, more preferably of at least 250 HV, and even more preferably of at least 300 HV. Said hardness (i.e. final hardness) is more particularly the one determined on the metal alloy obtained after the steps i, ii and optionally iii.

[0069] Another advantage is that the alloy obtained before the step ii can have a hardness of at least 200 HV. Said hardness (i.e. raw hardness) is more particularly the one determined on the alloy obtained in step i, or in other words, before step ii.

2.4. Results

[0070] In order to show the effects of the present invention, a comparative example has been performed (Metal alloy 6), and is gathered in the below table 6.

[0071] The amounts in Table 6 are expressed in weight percent (wt%) over the total weight of the metal alloy.

Table 6

Metal alloy 6	Au	Ag	Cu	Total
Weight percent (wt%)	58.5	26.5	15.0	100

[0072] The preparation of said Metal alloy 6 is similar to the preparation described in the above item 1, except that the rolling step (step ii) is of 75%.

[0073] The results are gathered in the following Table 7.

Table 7

	Metal alloy 1	Metal alloy 2	Metal alloy 3	Metal alloy 4	Metal alloy 5	Metal alloy 6
Entropy	1.47R	1.29R	1.47R	1.52R	1.29R	0.99R
ΔE	2.57	3.66	Not measured	Not measured	1.02	3.53
Raw hardness	230	150	194	188	228	175
Final hardness	330	320	253	237	246	260

Claims

1. Metal alloy comprising at least four metallic elements different from gold (Au), each of said metallic elements being in an amount from 1.0 to 55.0 atomic percent, **characterized in that** the metal alloy further comprises gold (Au) in an amount of at least 58.3 % by weight over the total weight of the metal alloy.

2. Metal alloy according to claim 1, **characterized in that** the metal alloy comprises at least 75.0 % by weight of gold (Au), over the total weight of the metal alloy.

3. Metal alloy according to any one of the preceding claims, **characterized in that** the metal alloy comprises from 5.0 to 30.0 atomic percent of each of said four metallic elements.

4. Metal alloy according to any one of the preceding claims, **characterized in that** the four metallic elements are selected among silver (Ag), aluminum (Al), manganese (Mn), copper (Cu), palladium (Pd), iron (Fe), chromium (Cr), platinum (Pt), and cobalt (Co).

5. Metal alloy according to claim 4, **characterized in that** the four metallic elements are copper (Cu), silver (Ag), manganese (Mn), and aluminum (Al).

6. Metal alloy according to claim 4, **characterized in that** the four metallic elements are palladium (Pd), silver (Ag), chromium (Cr), and iron (Fe).

7. Metal alloy according to claim 4, **characterized in that** the four metallic elements are silver (Ag), chromium (Cr), palladium (Pd), and cobalt (Co).

8. Metal alloy according to claim 4, **characterized in that** the four metallic elements are silver (Ag), cobalt (Co), palladium (Pd), and iron (Fe).

9. Metal alloy according to claim 4, **characterized in that** the four metallic elements are silver (Ag), platinum (Pt), palladium (Pd), and iron (Fe).

10. Metal alloy according to any one of the preceding claims, **characterized in that** the gold (Au) has a purity of at least 99.5 %, and more preferably of at least 99.9 %.

11. Process of manufacturing a metal alloy according to any one of the preceding claims, **characterized in that** the process comprises the following steps:

i. forming a molten alloy comprising gold (Au) and the at least four metallic elements different from gold,
ii. cold rolling the alloy obtained in step i, and
iii. optionally, annealing the alloy obtained in step ii.

12. Time-piece or jewel having a part or a component comprising the metal alloy according to any one of claims 1 to 11.

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EUROPEAN SEARCH REPORT

Application Number
EP 19 30 6367

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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X A	US 2018/171436 A1 (VINCENT DENIS [CH] ET AL) 21 June 2018 (2018-06-21) * paragraphs [0002], [0020], [0037], [0044], [0045]; table 1 * -----	1-4, 10-12 5-9	TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	31 January 2020	Brown, Andrew

CATEGORY OF CITED DOCUMENTS

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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