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(54) **TARNISHING RESISTANT GOLD ALLOY AT 14K AND METHOD OF PRODUCTION THEREOF**

(57) An alloy, in particular for jewelry, characterized in that it comprises:
- Gold, in the amount comprised between 540‰ and 620‰ in weight;
- Copper, in the amount comprised between 360‰ and 415%o in weight;
- Palladium, in the amount comprised between 10%o and 30%o in weight;

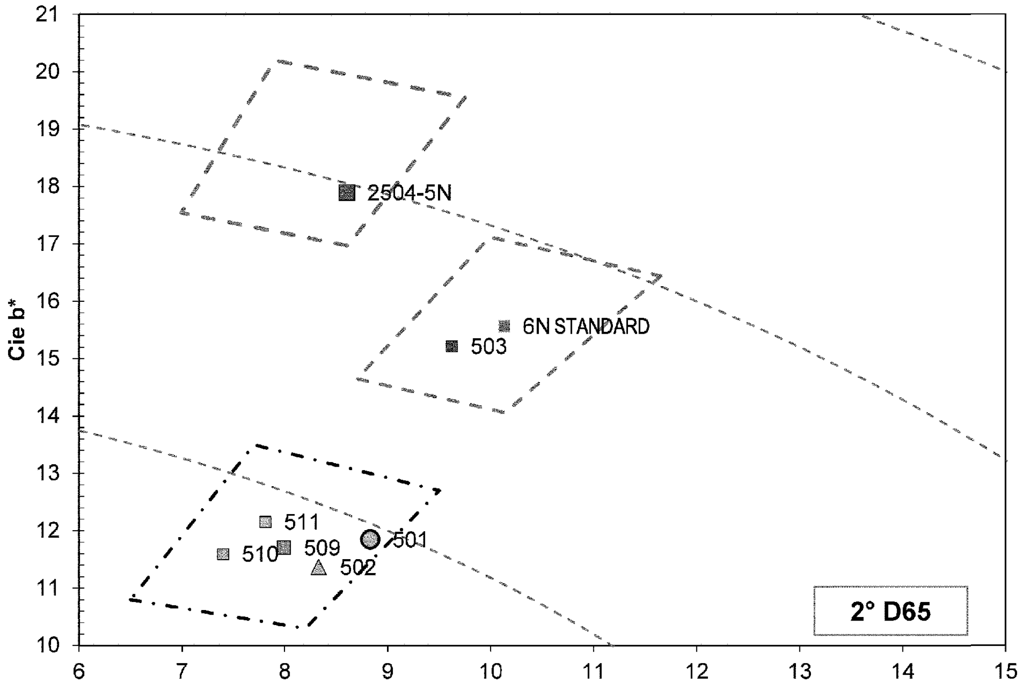

FIG.1

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Description

Field of the invention

[0001] The present invention refers to the field of Gold alloys and in particular refers to a Gold alloy with Gold title substantially equal to 14 carats (14K).

[0002] The present invention also refers to a method for the production of a Gold alloy.

[0003] The Gold alloy and the method for the production of Gold alloys according to the invention are an alloy and a method for the production of Gold alloys for jewelry and watchmaking applications respectively.

Background art

[0004] In the field of the jewelry and watchmaking, Gold is not used in pure form, since it is too ductile. For jewelry and watchmaking applications are typically used Gold alloys for jewelry or watchmaking, characterized by a higher hardness with respect to the Gold in pure form and/or with respect to low hardness or high ductility Gold alloys.

[0005] It is known that, generally, Gold alloys can undergo over time unwanted color alterations, following interactions with aggressive environments. These interactions bring to the creation of thin layers of reaction products, which staying adherent to the alloy surface, cause an alteration of the color and of the gloss (document "Observations of onset of sulfide tarnish on gold-base alloys"; JPD, 1971, Vol. 25, issue 6, page. 629-637).

[0006] Environments able to promote color alterations of Gold alloys are various and are linked to their applications.

[0007] Colors for Gold alloys can be uniquely measured in the CIELAB 1976 color space, which defines a color on the basis of a first L* parameter, a second a* parameter and a third b* parameter, wherein the first L* parameter identifies the brightness and adopts values comprised between 0 (black) and 100 (white) whereas the second a* parameter and the third b* parameter represent chromaticity parameters. In particular, in CIELAB 1976 color chart, the achromatic scale of greys is detected by points wherein a*=b*=0; positive values for the second parameter a* indicate a color tending the more to red as the higher the value of the second parameter is; negative values for the second parameter a* indicate a color tending the more to green as the value of the second parameter a* is a high absolute value, although negative; positive values for the third parameter b* indicate a color tending the more to yellow as the higher the value of the third parameter is; negative values for the third parameter b* indicate a color tending the more to blue as the value of the third parameter b* is a high absolute value, although negative. Furthermore, it is possible to transform the second a* parameter and the third b* parameter in polar parameters as defined:

$$C_{ab}^* = \sqrt{(a*^2 + b*^2)}$$

$$h_{ab*} = \tan^{-1}\left(\frac{b*}{a*}\right)$$

The C_{ab}^* parameter is defined as "chroma"; the higher the value of C_{ab}^* parameter is, the higher is the color saturation; the lower the value of C_{ab}^* parameter is, the lower is the color saturation, that will tend to the grey scale. To the knowledge of the Applicant, alloys with a Gold content higher than 750‰, which can be used as such as white or grey Gold alloys and do not require surface rhodium plating, arbitrarily show C_{ab}^* values <8. The parameter h_{ab*} identifies on the other hand the tonality of the color.

[0008] In particular, the ISO DIS 8654:2017 standard defines seven color designations as for the Gold alloys for jewelry. In particular, these alloys are defined according to the following table, wherein the color is defined on a standard reference specified between 0N and 6N.

Table 1

Color	Designation
0N	Yellow-green
1N	Dark yellow
2N	Light yellow
3N	Yellow
4N	Pink

(continued)

Color	Designation
5N	Red
6N	Dark red

[0009] For measuring the color of a Gold alloy, in particular, the ISO DIS 8654 standard specifies that the measuring instrument must comply with the CIE N° 15 publication.

[0010] The ISO DIS 8654:2017 standard also shows the nominal values L*, a*, b* as trichromatic coordinates for alloys of 0N-6N standard color, including the tolerances. Hereinafter is specified an abstract of the standard wherein are defined the chromatic limits of the alloys defined by the ISO DIS 8654:2017 standard as pink/red.

Table 2

Color	Trichromatic coordinates (2° observer)					
	Nominal values			Tolerances		
	L*	a*	b*	L* [MAX/Min]	a*	b*
4N	88.9	6.13	21.23	90.6	7.48	22.45
					6.63	19.44
				87.1	4.89	19.98
					5.48	23.06
5N	87.7	8.32	18.58	89.4	9.74	19.55
					8.62	16.97
				85.9	6.96	17.55
					7.89	20.19
6N	86.3	10.13	15.57	88.1	11.65	16.44
					10.14	14.06
				84.4	8.70	14.65
					9.99	17.12

[0011] In relation to the preceding table, it is then possible to obtain, within the CIELAB 1976 color space, a plurality of areas each of which represents the color spaces within which it is possible to assert that an alloy shows a 0N...6N color and more specifically a 5N-6N color. These areas are represented in details in figure 1.

[0012] The ISO DIS 8654:2017 standard also proposes chemical compositions recommended for each of the 0N-6N alloys. In particular, for pink/red alloys, the compositions are the ones specified in the table:

Table 3

Color	Chemical composition - % in weight		
	Au	Ag	Cu
4N	75.0	8.5 - 9.5	Remaining part
5N	75.0	4.5 - 5.5	
6N	75.0	0 - 1.0	

[0013] The Applicant has noted that the pink/red Gold alloys of known type show a substantial color instability, in particular when exposed to environments wherein there are chlorides or sulphides.

[0014] Variations of the color of a Gold alloy according to the color as defined on the CIE 1976 color chart and specified by the E=f (L*, a*, b*) coordinate, defined:

- L_0^* as first parameter in original conditions, at time to=0;
- a_0^* as second parameter in original conditions, at time to=0;
- b_0^* as third parameter in original conditions, at time to=0;

are defined in the following equation:

$$\Delta E(L^*, a^*, b^*) = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (Lb^* - b_0^*)^2}$$

[0015] It has also been noted that the human eye of a technician expert in precious materials is able to detect color variations ΔE (L*, a*, b*) >1.

[0016] In particular, the Applicant has noted that the 5N ISO DIS 8654:2017 Gold alloy in the formulation that uses the minimum reference value as for the content of Silver exposed to vapors of thioacetamide for 150 hours (according to the UNI EN ISO 4538:1998 standard), shows a variation of color ΔE (L*, a*, b*) equal to 5.6; when exposed to the action of an aqueous solution 50g/liter of sodium chloride (NaCl) at 35°C for 175 hours, the 5N Gold alloy shows a variation of color ΔE (L*, a*, b*) equal to 3.6.

[0017] There are also known jewelry alloys, comprising Gold with a title equal to or substantially equal to 14K. These Gold alloys are typically used to make jewels of value lower than those made with 18K or higher Gold alloys. In particular, among the alloys including Gold with a title equal to or substantially equal to 14K, there are known alloys containing Copper, suitable to appear with a pink or red color, according to a growing percentage of Copper in the alloy.

[0018] In alloys including Gold with title equal to or substantially equal to 14K, it is known that the presence of Copper has the drawback of being rather prone to vary color especially when the object of jewelry is worn and exposed to human sweating and/or saline environment. The same alloys, including Gold with a title equal to or substantially equal to 14K are known to have significant color variation even just after exposure to air.

[0019] For this reason, typically jewelry items made from alloys including Gold with a title equal to or substantially equal to 14K, in particular when including Copper, are covered with a plating with Gold alloys with a title significantly higher than 14K, typically for example 16K or 18K. This plating has some further drawbacks. A first drawback derives from the fact that it is difficult to realize a plating whose color is perfectly superimposable to that of the basic alloy with which the item of jewelry is made.

[0020] Furthermore, the plating of a jewelry item with high title Gold alloys is expensive, and significantly contributes to the increase in the production cost of the item not only because of the cost of the high title Gold alloy, but also because of the further necessary processing on the jewelry item, which incidentally for shapes of jewelry items of considerable complexity, may not be insignificant.

[0021] Finally, the plating, representing the surface layer of the item, is the portion the most subject to wear or anyhow removal; with the removal of the plating, the item of jewelry may have exposed portions of alloy with Gold title equal to or substantially equal to 14K, which - exposed to chemically aggressive environments - may have different color than the portions that vice versa still carry the plating alloy.

[0022] The purpose of the present invention is therefore to describe a Gold alloy, particularly for jewelry and watch-making, with a Gold title equal to or substantially equal to 14K, which solves the above described drawbacks, in particular being not very prone to turn color when exposed to environments with air, Thioacetamide or NaCl in solution.

[0023] The purpose of the present invention is also to describe a method of production of an alloy containing Gold with a title equal to or substantially equal to 14K, which solves the above described drawbacks.

[0024] The purpose of the present invention is finally to describe an item of jewelry or part of an item for jewelry, made with the alloy object of the invention, which does not show the above described drawbacks.

Summary

[0025] These and other purposes are obtained by the alloy and by the method of production thereof described in the following aspects. The following aspects may be combined with each other and/or with portions of the description and claims. The aspect dependencies, when present, are to be intended as preferred and non-limiting.

[0026] Forms a first aspect of the invention an alloy, in particular for jewelry, characterized in that it comprises:

- Gold, in the amount comprised between 540‰ and 620‰ in weight;
- Copper, in the amount comprised between 360‰ and 415‰ in weight;

- Palladium, in the amount comprised between 10‰ and 30‰ in weight;

Said alloy in particular can consist of:

- Gold, in the amount comprised between 540‰ and 620‰ in weight;
- Copper, in the amount comprised between 360‰ and 415‰ in weight;
- Palladium, in the amount comprised between 10‰ and 30 ‰ in weight, and, optionally, at least one among Silver in the amount lower than or equal to 80‰ in weight, Zinc in the amount lower than or equal to 80‰ in weight, Indium in the amount lower than or equal to 20‰ in weight, Tin in the amount lower than or equal to 20‰ in weight, Iron in the amount lower than or equal to 15‰ in weight, Gallium in the amount lower than or equal to 10‰ in weight, Iridium or Ruthenium in the amount lower than or equal to 0.5‰ in weight, Rhenium in the amount lower than or equal to 0.1‰ in weight.

[0027] According to the purposes of this invention, as "jewelry alloy" is intended an alloy, in particular a Gold alloy, in which there are no materials toxic to humans and the formulation of which is suitable for, specifically designed for, making jewels, or parts thereof. In particular, a jewelry alloy is an alloy that shows, in absence of work hardening, a hardness, measured on a Vickers scale and in particular with the HV5 method, higher than 95, preferably higher than 98.

[0028] According to a 2° non-limiting aspect, the alloy according to the first aspect is a Gold alloy characterized by a pearly red color. According to the present invention, as "pearly red" is intended a color that, arbitrarily, on the a*, b* color plan according to the CIE 1976 color chart, is not comprised in the spaces defined by the ISO DIS 8654:2017 standard and is enclosed in a polygon at least defined by the following points (Fig. 1):

Table 4

Color	Trichromatic coordinates (2° observer)					
	Nominal values			Tolerances		
	L*	a*	b*	L* [MAX/Min]	a*	b*
pearly red	86.1	8	11.60	87.8	6.5	10.8
					8.2	10.3
				84.3	9.5	12.7
					7.7	13.5

[0029] According to a 3° non-limiting aspect, the alloy according to a first or second aspect is a tarnishing resistant alloy and/or shows a color variation in NaCl saline solution lower, optionally after a time equal to at least 24h of exposure, lower than the color variation underwent by a reference alloy with a title of Silver equal to 40‰ and/or lower than the 5N alloy according to the ISO DIS 8654:2017 standard.

[0030] According to a 4° non-limiting aspect, the alloy depending on one or more of the preceding aspects, comprises Palladium in the amount comprised between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight.

[0031] According to a 5° non-limiting aspect, the alloy according to one or more of the preceding aspects, comprises also Iron in the amount comprised between 2‰ in weight and 15‰ in weight, more preferably comprised between 4‰ in weight and 13‰ in weight, even more preferably between 5‰ in weight and 10‰ in weight.

[0032] According to a 6° non-limiting aspect, the alloy according to one or more of the preceding aspects is a ternary or quaternary alloy, and/or the sum of the amounts of Gold, Copper and Palladium is at least equal to 910‰ in weight.

[0033] According to the present invention, as ternary or quaternary Gold alloy is intended an alloy wherein there are 3 or 4 components respectively, the amount of which is not negligible, and in particular higher than 2‰ in weight and more preferably higher than 1‰ in weight. In other words, quaternary or quinary alloys do not comprise components in excess of 2‰ in weight and more preferably 1‰ in weight in addition to those explicitly mentioned.

[0034] According to a 7° non-limiting aspect, the alloy according to the sixth aspect shows a sum of the amounts of Gold, Copper and Palladium at least equal to 950‰ in weight, more preferably 960‰ in weight, even more preferably 970‰ in weight.

[0035] According to a 8° non-limiting aspect, in the alloy according to one of the preceding aspects, when depending on the 5° aspect, the sum of the amounts of Palladium and Iron is equal to or lower than 37‰ in weight, more preferably lower than 35‰ in weight.

[0036] According to a 9° non-limiting aspect, in the alloy according to one of the preceding aspects, when depending on the 5° aspect, the Iron is comprised in the amount comprised between 5‰ and 10‰.

[0037] According to a 10° non-limiting aspect, in the alloy according to one or more of the preceding aspects, the Gold is present in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and Palladium is comprised between 12%0, more preferably between 15‰ in weight, and 27‰, more preferably 25‰ in weight.

[0038] According to a 11° non-limiting aspect, in the alloy according to one or more of the preceding aspects, when depending on the 5° aspect, the Gold is present in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and the sum of Palladium and Iron is comprised between 23‰ and 27‰, even more preferably substantially equal to 25‰.

[0039] According to a 12° non-limiting aspect, in the alloy according to one of the aspects from 1° to 3° and/or from 5° to 9°, the Palladium is present in the amount comprised between 13‰ in weight and 17‰ in weight, preferably between 14‰ in weight and 16‰ in weight and even more preferably in the amount substantially equal to 15‰ in weight.

[0040] According to a 13° non-limiting aspect, in the alloy according to the 12° aspect and according to the 5° aspect, the Gold is present in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and the sum of the amounts of Palladium and Iron is comprised between 25‰ and 30‰.

[0041] According to a 14° non-limiting aspect, in the alloy according to the 12° aspect and according to the 5° aspect, the Gold is present in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and the sum of the amounts of Palladium and Iron is comprised between 30‰ and 35‰.

[0042] According to a 15° non-limiting aspect, the alloy according to the 6° aspect comprises also Silver in the amount lower than 40‰ in weight, and/or Zinc in the amount lower than 40‰ in weight or Silver and Zinc the sum of respective amounts in weight is lower than 40‰.

[0043] In particular, according to a 16° non-limiting aspect, the alloy according to the 10° aspect, is free from Iron.

[0044] According to a 17° non-limiting aspect, the alloy according to one or more of the preceding aspects, is an alloy whose color on the CIELAB1976 color chart shows a coordinate a* comprised in the range [6.5 - 9.5] and a coordinate b*<13.5, preferably comprised in the range [10 - 13,5].

[0045] According to a 18° non-limiting aspect, the alloy according to one or more of the preceding aspects is an alloy characterized by the absence of Vanadium and other materials capable to create carbides and oxides, in particular free from Magnesium, Silicon, Titanium, Tungsten, Molybdenum, Niobium, Tantalum, Zirconium, Yttrium, Germanium. Thanks to this aspect, it is possible to prevent the creation of carbides.

[0046] According to a 19° non-limiting aspect, the alloy according to one or more of the preceding aspects, is a Gold alloy for jewelry free from Nickel, Cobalt, Arsenic and Cadmium. Thanks to this aspect, the alloy is a Gold alloy wearable by subjects whose allergic tolerance is significantly low.

[0047] According to a 20° independent aspect, it is also object of the invention a method for the production of a Gold alloy; said method is characterized in that it comprises:

a) a step (hereinafter defined as homogenization) wherein all the pure elements constituting the alloy are melted in such a way as to obtain an homogeneous solution or mixture; this mixture comprises in weight at least:

- Gold, in the amount comprised between 540‰ and 620‰ in weight;
- Copper, in the amount comprised between 360‰ and 415‰ in weight;
- Palladium, in the amount comprised between 10‰ and 30‰ in weight;

for creating a mixture; and

b) a step of introduction of the mixture in a melting pot, and a subsequent melting through heating until melting.

[0048] According to a 21° non-limiting aspect, depending on the preceding 20° aspect, said step comprises mixing in particular Palladium in the amount comprised between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight.

[0049] According to a 22° non-limiting aspect, depending on one or more of the preceding 20°-21° aspects, the method comprises in particular mixing, in addition to the preceding elements, also Iron in the amount comprised between 2‰ and 15‰ in weight, more preferably comprised between 4‰ and 13‰ in weight, even more preferably between 5‰ and 10‰ in weight.

[0050] According to a 23° non-limiting aspect, in the alloy according to one or more of the preceding aspects from 20° to 22°, the sum of the amounts of Gold, Copper and Palladium is at least equal to 910‰ in weight.

[0051] According to a 24° non-limiting aspect, depending on the preceding 23° aspect, the step of mixing comprises the mixing of Gold, Copper and Palladium in the amount at least equal to 950‰ in weight, more preferably 960‰ in weight and/or the sum of the amounts of Gold, Copper and Palladium is at least equal to 950‰ in weight, more preferably 960‰ in weight.

[0052] According to a 25° non-limiting aspect, in the alloy according to the 22° aspect, comprises the mixing of the above mentioned elements with the amount of the sum of Palladium and Iron equal to or lower than 37‰ in weight, more preferably lower than 35‰ in weight.

[0053] According to a 26° non-limiting aspect, depending on the above mentioned 22° aspect or on one of its dependent aspects, the method comprises the mixing of Iron in the amount comprised between 5‰ and 10‰ in weight.

[0054] According to a 27° non-limiting aspect, when depending on one or more of the 18° aspects and following, the method comprises the mixing of Gold in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper in the amount comprised between 370‰ and 405‰ in weight and Palladium in the amount comprised between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight.

[0055] According to a 28° non-limiting aspect, depending on one or more of the preceding aspects when depending on the 22° aspect, the method comprises the mixing of Gold in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper in the amount comprised between 370‰ and 405‰ in weight and the sum of Palladium and Iron in the amount comprised between 23‰ and 27‰, even more preferably substantially equal to 25‰ in weight.

[0056] According to a 29° non-limiting aspect, depending on one or more of the preceding aspects from 18° to 20° and 22°, the method comprises the mixing of Palladium in the amount comprised between 13‰ in weight and 17‰ in weight, preferably between 14‰ and 16‰ in weight and even more preferably in the amount substantially equal to 15‰ in weight.

[0057] According to a 30° non-limiting aspect, depending on the 22° and 29° aspects, the method comprises the mixing of Gold in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper in the amount comprised between 370‰ and 405‰ in weight, Palladium and Iron in the amount of which the sum is comprised between 25‰ and 30‰ in weight.

[0058] According to a 31° non-limiting aspect, depending on the 22° and 29° aspects, the method comprises the mixing of Gold in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ and 595‰ in weight, and Copper in the amount comprised between 370‰ and 405‰ in weight, and the sum of Palladium and Iron in the amount comprised between 30‰ and 35‰ in weight.

[0059] According to a 32° non-limiting aspect, the alloy according to one or more of the preceding aspects starting from the 20°, the method comprises the obtaining of an alloy whose color, optionally at the moment of the cooling, on the CIELAB1976 color chart shows a coordinate a* comprised in the range [6.5 - 8.8] and a coordinate b*<13, preferably comprised in the range [10 - 13].

[0060] According to a 33° non-limiting aspect, depending on one or more of the preceding aspects starting from the 20°, the method excludes the mixing of Vanadium and other materials capable to create carbides and oxides, in particular free from Magnesium, Silicon, Titanium, Tungsten, Molybdenum, Niobium, Tantalum, Zirconium, Yttrium, Germanium. The absence of said carbides or oxides, in particular but non-limiting after the processing, makes the Gold alloy suitable for applications of jewelry and watchmaking where polishing or diamond polishing of finished items is required.

[0061] According to a 34° non-limiting aspect, depending on one or more of the preceding aspects starting from the 20°, depending on one or more of the preceding aspects starting from the 33°, the method excludes the mixing of Nickel, Cobalt, Arsenic and Cadmium. Thanks to this aspect, the alloy is a Gold alloy wearable by subjects whose allergic tolerance is significantly low.

[0062] According to a 35° non-limiting aspect, depending on one or more of the aspects starting from 20°, said homogenization is a discontinuous melting, comprising a step of casting wherein the melted material is casted in a refractory mold or refractory or metallic ingot.

[0063] According to a 36° aspect, depending on one or more of the aspects starting from 20°, during said melting, the melting pot is subject to a gas controlled atmosphere and in particular is subject, at least temporarily, to a vacuum condition.

[0064] According to a 37° non-limiting aspect, depending on one or more of the aspects starting from 20°, during said casting step, said melting pot is subject to a controlled atmosphere, to pressures lower than the environmental one.

[0065] According to a 38° non-limiting aspect, depending on one or more of the aspects starting from 20°, said controlled atmosphere is an inert gas, preferably argon and/or said pressure is a pressure lower than 800mbar, preferably lower than 700mbar.

[0066] According to a 39° non-limiting aspect, depending on one or more of the aspects starting from 20°, said gas is a reducing gas, preferably a hydrogen-nitrogen mixture and/or said pressure is a pressure lower than 800mbar, preferably lower than 700mbar.

[0067] According to a 40° non-limiting aspect, said melting is a continuous melting, comprising a step of melting and homogenization in a graphite pot and a subsequent melting step wherein the melted alloy is casted in a die realized in graphite and wherein said alloy is an alloy of metals without chemical affinity to graphite and more specifically, in particular at least free from Vanadium, Magnesium, Silicon, Titanium, Tungsten, Molybdenum, Niobium, Tantalum, Zirconium, Yttrium, Germanium.

[0068] The absence of elements without chemical affinity to graphite, allows an excellent flow of the melted alloy within the die and facilitates the extraction thereof after solidification. On the contrary, the presence of elements with chemical affinity to graphite, causes a gripping effect of the alloy to the die, preventing the extraction. Furthermore, the absence of carbides and oxides makes the Gold alloy suitable for applications of jewelry and watchmaking where polishing or diamond polishing of finished items is required.

[0069] According to a 41° non-limiting aspect, depending on one or more of the aspects starting from 20°, after the continuous or discontinuous melting, said alloy is subject to a cooling step followed by one or more hot or cold plastic deformation step and one or more thermal treatments.

[0070] According to a 42° aspect, it is also object of the present invention an item of jewelry, comprising a Gold alloy according to one or more of the preceding aspects concerning said Gold alloy. In particular, forms an object of the present invention an item of jewelry, realized at least partially through a Gold alloy according to one or more of the aspects here described.

[0071] According to a 43° aspect, depending on the preceding aspect, said item of jewelry comprises a jewel or a watch or a watch bracelet or a movement or part of a mechanical movement for watches.

[0072] According to a 44° aspect, depending on the preceding aspect, said watch or mechanical movement for watches are configured for being respectively worn or installed in wristwatches.

[0073] According to a 45° aspect, it is realized a method of production of an item for jewelry or part of an item for jewelry, said method being characterized in that it comprises one or more steps of mechanical processing of a Gold alloy according to one or more of the aspects from 1° to 19°.

[0074] According to a 46° aspect, that can be combined with one or more of the preceding aspects, the Gold alloy is free from secondary phases, and/or is a homogeneous alloy, and/or is a crystalline alloy, optionally 100% crystalline.

[0075] According to the present invention, as "free from secondary phases" or "free from second phases" is intended an alloy free from elements that can generate said second phases, in particular in a proceeding of melting and subsequent solidification without other thermal treatments; second phases that create in the liquid phase and remain downstream of the alloy solidification, are harmful second phases, for example carbides and/or oxides that during the polishing step are visible at naked eye on the surface of the polished item, and that then prevent to obtain items of high surface quality, compatible with the needs required in the high jewelry field. It is possible to expose the alloy to thermal treatment processes, able to give it a hardening, so that due to precipitation subtle precipitates can be present, as results of said thermal treatment; in this case these are precipitates that prevent from the movement of displacement by increasing the mechanical properties in the material, and contrasting the incidence of deformations in the items realized with the present alloys.

Description of drawings

[0076] The invention is hereinafter described in preferred and non-limiting embodiments, whose description is associated to the attached figures wherein:

- Figure 1 shows a portion of CIELAB 1976 color space according to the coordinates L*, a*, b* wherein it has been detected an area corresponding to color intervals or tolerances admissible for Gold alloys according to the 5N and 6N ISO DIS 8654:2017 standard and wherein it is shown the typical color position for alloys object of the present invention;
- Figure 2 shows a color variation chart according to the time of exposure to a saturated 50g/L NaCl solution for part of the alloys object of the present invention, in relation to the color variation gained by the 5N alloy according to the ISO composition used as reference sample and in relation to the color variation of a reference Gold, Silver and Copper red ternary 14K alloy (LRS 503, defined hereinafter in Tab. 6);
- Figure 3 shows a color variation chart according to the time of exposure to Thioacetamide according to UNI EN ISO 4538 for part of the alloys object of the present invention, in relation to the color variation gained by the 5N alloy according to the ISO composition used as reference sample and in relation to the color variation of a reference Gold, Silver and Copper red ternary 14K alloy (LRS 503, defined hereinafter in Tab. 6);

Detailed description of the invention

[0077] It is an object of the present invention a family of Gold alloys, in particular for jewelry, with Gold title substantially comprised between 13K and 15K that have tarnishing resistance characteristics.

[0078] The alloys that are described in the present invention have been tested in terms of resistance to color variation (tarnishing) in environments comprising Thioacetamide and NaCl solutions (sodium chloride). In this description, any reference to tests carried out in an environment comprising Thioacetamide is made according to the indications of the UNI EN ISO4538:1998 standard. In order to carry out the tests, according to the present invention, the samples are exposed to vapours of Thioacetamide CH_3CSNH_2 in an atmosphere with relative humidity of 75% kept through the presence of a saturated solution of sodium acetate trihydrate $CH_3COONa \cdot 3H_2O$ in a test chamber with a capacity comprised between 2 and 20 litres and wherein all the materials used for the construction of the chamber itself are resistant to volatile sulphides and do not emit any gas or vapour capable of influencing the results of the test.

[0079] With regard to the assessment of the resistance to corrosion and color variation in environments characterized by the presence of Sodium Chloride solutions, the tests have been carried out by immersing the samples of a Gold alloy in a 50g/L NaCl solution at neutral pH, thermostated at 35°C.

[0080] In order to obtain tarnishing resistance properties, in particular in environments comprising solutions of Thioacetamide and NaCl according to the above described standards and also to obtain a Gold alloy whose color, measured according to the ISO DIS 8654:2017 standard is contained in the color space defined as "pearly red", the Applicant has conceived a family of Gold alloys comprising:

- Gold, in the amount comprised between 540‰ and 620‰ in weight;
- Copper, in the amount comprised between 360‰ and 415‰ in weight;
- Palladium, in the amount comprised between 10‰ and 30‰ in weight;

[0081] More in particular, preferably but in a non-limiting extent, the Gold alloy according to the invention may consist of: Gold, in the amount comprised between 540‰ and 620‰ in weight; Copper, in the amount comprised between 360‰ and 415‰ in weight; Palladium, in the amount comprised between 10‰ and 30 ‰ in weight, and, optionally, at least one among Silver in the amount lower than or equal to 80‰ in weight, Iron in the amount lower than or equal to 80‰ in weight, Zinc in the amount lower than or equal to 80‰ in weight, Indium or Ruthenium in the amount lower than or equal to 0.5‰ in weight, Rhenium in the amount lower than or equal to 0.1‰ in weight, Tin in the amount lower than or equal to 20‰ in weight.

[0082] According to the present invention, with "tarnishing" is intended a surface corrosion of the Gold alloy that causes a variation in the alloy color.

[0083] The family of Gold alloys object of the invention comprises at least ternary alloys, and more in particular ternary or quaternary alloys. Therefore, the number of elements that are included in a not insignificant amount in the family of Gold alloys object of the invention is at least equal to 3 and, preferably, not higher than 4, although quinary formulations may still be possible and include elements not included in the preceding table.

[0084] The Applicant has carried out various experiments for assessing the resistance to tarnishing and the so obtained color of the alloys, and in particular has carried out experiments on the specific embodiments indicated in the following table:

Table 5

	Nominal composition %]							
Lega	**LRS**	**Au**	**Ag**	**Cu**	**Pd**	**Fe**	**In**	**Total**
14 K	**501**	585.5		394.5	20			1000
	502	585.5		389.5	25			1000
	509	585.5		389.5	20	5		1000
	510	585.5		384.5	20	10		1000
	511	585.5		389.5	15	10		1000

[0085] In the preceding table, as in the other tables of the present description, where the boxes are empty, it is intended a zero percentage of the relevant element.

[0086] The alloys according to the preceding formulations are preferred and non-limiting examples of Gold alloy for jewelry with a title equal to or substantially equal to 14K. The tarnishing resistance tests carried out by the Applicant and reported below have been carried out with respect to a reference alloy, in particular a reference ternary alloy comprising Gold, Copper and Silver, not optimized then for tarnishing resistance due to its composition, hereinafter indicated:

Table 6

Reference alloy nominal composition %]						
LRS 503	Au	Ag	Cu	Pd	Fe	Total
	585.5	40	374.5			1000

[0087] The alloys according to the family generally described as the object of the invention and, consequently, the specific realizations described in table 5 are realizations preferably characterized by the absence of Silver. Silver is known to be an element that in these alloys helps to increase the hardness of the alloy. As an example, the LRS 503 alloy used as reference test, in the absence of work hardening, has a hardness according to HV5 equal to 130, equal to 173 with 25% work hardening, equal to 230 with 50% work hardening and equal to 258 with 75% work hardening. In particular, for the alloys listed in Table 5, it has been searched an alternative solution to Silver, which could also help to keep the hardness of the specific formulation of alloy suitable for jewelry applications, such as to make the formulation "for jewelry" as defined in the preceding definition, avoiding the tendency to tarnishing that Silver helps to bring for alloys where it is contained.

[0088] The following table shows the hardnesses obtained for the specific alloy formulations according to the present invention, as well as for the LRS 503 alloy used as reference test.

Table 7

	% work hardening			
HV5	**0**	**25**	**50**	**75**
501	**127**	**173**	**220**	**240**
502	**119**	**175**	**231**	**244**
503	**130**	**173**	**230**	**258**
509	**129**	**171**	**225**	**242**
510	**125**	**171**	**232**	**248**
511	**135**	**180**	**235**	**251**

[0089] The Applicant has observed that the specific formulations of Gold alloy described in table 7 have hardness, in particular at the annealed stage, compatible with that of alloys for jewelry according to the present invention. In particular, the LRS 509 and LRS 511 formulations are respectively the closest to the behavior in terms of hardness possessed by the LRS 503 (whose alignment in the table is offset for ease of representation) used as reference test and even better, at least until the work hardening equal to 50% with respect to the behavior obtained by the LRS 503 alloy. The Applicant has then observed that for Gold alloys with Gold title equal to or substantially equal to 14K, and in particular for the specific tested embodiments, it is possible to replace Silver with mixtures of Palladium and Iron, for obtaining equal or higher performances in terms of hardness, also with lower quantities of extra elements with respect to Gold and Copper. In fact, specifically for the case of the LRS 511 formulation, the sum of the amounts of Palladium and Iron is equal to 35‰, while in the case of the LRS 503, used as reference test, the amount of Silver was equal to 40‰.

[0090] From an observation of the behavior in terms of hardness between the LRS 509, LRS 510 formulation and the LRS 511 formulation, it has also been observed that is determining, in the increase of hardness, the content of Iron and Copper, taken as a sum.

[0091] The Applicant has observed as it will be better described hereinafter that all the alloys object of the invention and belonging to the above mentioned family, and in particular but non-limiting to the alloys object of table 5 have better performances in Air, Thioacetamide and NaCl solution under the above mentioned conditions, in terms of resistance to color variation, with respect to what can be obtained with the LRS 503 alloy used as reference test. The graphs in Figure 2 and Figure 3 respectively illustrate the evolution of the color of some specific alloy formulations as the number of hours of exposure to NaCl saline solution and Thioacetamide increases, as for the above indicated specifications.

[0092] All the alloys according to the general formulation, and in particular all the specific realizations of the alloys according to table 5 have a better behavior, both in NaCl solution and in Thioacetamide, with respect to the LRS 503 alloy used as reference test. This shows that the elimination of Silver, among other things, is beneficial for reducing the trend of the alloy to turn color when exposed to chemically aggressive environment. In fact, although the alloy used as a reference test has a color that is not compatible with that of the alloys object of the invention, the latter have a significantly lower trend to change color.

[0093] Surprisingly, the Applicant has observed that the alloys according to the general formulation above mentioned and in particular all the specific embodiments of alloys according to table 5 have a behavior in NaCl saline solution as for the above mentioned specifications even better that the behavior obtained by 5N alloy according to the ISO standard, whose Gold content is significantly higher, being as a matter of fact equal to 18K.

[0094] In particular, the Applicant has observed that the optimization of the alloy behavior in terms of tarnishing is optimized - in the ranges identified in the preceding family, for Palladium values comprised within the following range: [8‰ - 32‰] in weight, and even more preferably for Palladium values within the range of [10‰ - 30‰] in weight.

[0095] In particular, it has been observed that in NaCl saline solution the absolute best behavior in terms of resistance to color variation, in particular for exposures higher than 5h, is the one of the LRS 502 alloy, which includes the highest Palladium content among the specific formulations of table 5 and is characterized by the absence of Iron; although Iron is known for optimizing the performances of alloys in an environment containing Thioacetamide (WO2014/0872216 A1), the Applicant has surprisingly found that the LRS 509 alloy, as well as the LRS 510 alloy, although both of them have Iron in the measure of 5‰ and 10‰ respectively have performances substantially similar to that of the alloy according to the LRS 502 formulation and better than that of the alloy according to the LRS 501 formulation, ternary, which shows only Palladium in the amount of 20‰. Experimental tests carried out show that sums of Iron and Palladium equal to or substantially equal to 25‰ in a ternary Gold-Copper-Palladium or quaternary Gold-Copper-Palladium-Iron alloy, lead to an optimization of the characteristics in terms of resistance to color variation.

[0096] The following table describes the color variation characteristics ΔE (L*, a*, b*) according to the exposure time in NaCl saline solution.

Table 8

	Time (h)			
Δ*E*	**0**	**2**	**6**	**24**
5N	0.00	1.58	1.85	2.07
LRS 501	0.00	0.43	0.95	1.39
LRS 502	0.00	0.55	0.70	1.00
LRS 503 (Ref.14K)	0.00	1.37	1.59	1.80
LR**S 509**	0.00	0.37	0.75	1.08
LRS 510	0.00	0.71	0.80	1.14
LRS 511	0.00	0.64	0.82	1.35

[0097] Vice versa, as represented in the diagram of figure 3, in Thioacetamide an alloy such as the ones object of the present invention cannot present a resistance to the variation of color equal to the one which is typical of an 18K Gold alloy such as the 5N ISO, which after 24 hours of exposure presents a variation of color ΔE(L*, a*, b*) substantially equal to 3.6, while all the tested alloys - and more generally the alloys according to the general formulation above expressed - have a color variation under the same conditions higher than ΔE(L*, a*, b*)>4. However, the alloys object of the invention have a significantly better behavior than the LRS 503 alloy used as reference test, which after 24 hours of exposure in Thioacetamide has a color variation equal to 6.20.

[0098] The alloy with the best behavior in Thioacetamide is the alloy according to the LRS 511 formulation, which after 24 hours of exposure presents in particular a color variation ΔE(L*, a*, b*) = 4.56. From a comparison with the alloy according to the LRS 510 formulation, which has the same Iron content, but a color variation that under the above mentioned conditions is equal to ΔE(L*, a*, b*) = 5.80 it is inferred that with the same Iron content, the increase of Palladium content contributes to worsen the performances of the alloy in terms of color variation resistance in Thioacetamide.

[0099] The following table describes the color variation characteristics ΔE (L*, a*, b*) according to the exposure time in Thioacetamide.

Table 9

Time (h)					
	0	**2**	**4**	**8**	**24**
5N	0.00	0.67	1.82	2.39	3.61

(continued)

Time (h)					
	0	**2**	**4**	**8**	**24**
LRS 501	0.00	0.90	1.30	3.90	5.22
LRS 502	0.00	0.77	1.45	3.88	5.35
LRS 503 (Ref.14K)	0.00	0.84	2.06	4.68	6.20
LRS 509	0.00	0.58	1.77	3.98	5.40
LRS 510	0.00	0.45	1.54	4.01	5.80
LRS 511	0.00	0.73	1.42	3.26	4.56

[0100] In order to reduce the risk that the inclusion of third-party elements in the preceding alloy family may lead to unpredictable behaviors, the Applicant has observed that the alloy must be preferably ternary or quaternary, with the necessary presence of Palladium and with the sum of the amounts of Gold, Copper and Palladium at least equal to 900‰ in weight. The remaining 100‰ in weight can be of different materials, including Silver or Zinc or combinations of Silver or Zinc in order to vary at least the specific color of the alloy while remaining within the color previously defined as "pearly red".

[0101] As it can be seen from the graph in figure 1, all the alloys object of the invention, in particular those included in the preceding general formulation and, even more in particular, the specific embodiments of table 5, are enclosed in the box generally defined as "pearly red". The following table shows the values of coordinates L*, a*, b* for the alloys object of the invention and for the alloy used as reference test.

Table 10

	2° Observer		
	L*	**a***	**b***
501	85.4	8.8	11.9
502	84.9	8.3	11.4
503 (ref. 14k)	**87.1**	**9.6**	**15.2**
509	85.4	8.0	11.7
510	85.7	7.4	11.6
511	85.6	7.8	12.2

[0102] From the preceding Table 10, it is clear that the LRS 503 alloy used as reference test is the only one with a significantly different color with respect to the others, and that it is not "pearly red" according to the present invention, since it falls within the tolerance limits defined for alloys whose color complies with the 6N ISO standard.

[0103] In particular, all the embodiments specifically identified in Table 5 are specific optimized embodiments taken from a subfamily of alloys in which the sum of the amounts of Gold, Copper and Palladium is at least equal to 960‰ in weight and, even more preferably 970‰ in weight; alloys with this last characteristic have an assimilable behavior in the complex, observing the color variations in air, in Thioacetamide and in NaCl solution.

[0104] In developing the alloys object of the specific formulations of Table 5, alloys were conceived according to a first subfamily that comprises Palladium in the amount between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight.

[0105] Furthermore, starting from the alloys according to the general formulation above mentioned, alloys have been developed that include Iron in an amount comprised between 2‰ in weight and 15‰ in weight, more preferably comprised between 4‰ in weight and 13‰ in weight, and even more preferably between 5‰ in weight and 10‰ in weight.

[0106] In particular, are part of the general formulation, and also of the alloys according to table 5, formulations whose sum of the amounts of Palladium and Iron is equal to or less than 37‰ in weight, more preferably less than 35‰ in weight. The presence of Iron and Palladium in an amount lower than 37‰ in weight, more preferably lower than 35‰, contributes to optimize the resistance to tarnishing in Thioacetamide and in saline solution of NaCl. In particular, when Iron is comprised in the amount comprised between 5‰ and 10‰, especially with Palladium in the amount equal to or substantially equal to 20‰, the performances of the alloys in Thioacetamide have improved.

[0107] As part of the family in the general formulation of the invention, and within which are also included the specific formulations of the Gold alloy according to table 5, is highlighted in particular a subfamily of alloys wherein Gold is present in the amount between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight, and Palladium is comprised between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight. All these alloys have a better performance in Thioacetamide and NaCl saline solution than the reference alloy LRS 503 in terms of resistance to color variation.

[0108] A subfamily of alloys has also been studied in which Gold is present in the amount between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight, and the sum of the amounts of Palladium and Iron is comprised between 23‰ and 27‰, even more preferably substantially equal to 25‰. The presence of Palladium and Iron in the amounts above described contributes to optimize the performances of the alloy in saline solution of NaCl, in particular for low Iron contents, in a measure equal to or substantially equal to 5‰.

[0109] Where Iron is also present, it is possible to create families of alloys in which Gold is present in amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and the sum of Palladium and Iron is comprised between 25‰ and 30‰.

[0110] In another different case, Palladium is present in the amount between 13‰ and 17‰ in weight, preferably between 14‰ and 16‰ in weight and even more preferably in the amount substantially equal to 15‰ in weight. In fact, in particular if the amount of Iron is substantially equal to 10‰, the performances of the alloy in Thioacetamide are substantially maximized. Therefore, with maximized performances, it is possible to realize Gold alloys for jewelry in which Gold is present in amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and the sum of Palladium and Iron is comprised between 30‰ and 35‰.

[0111] It is alternatively possible to realize Gold alloys according to the above mentioned general formulation wherein Silver is in the amount lower than 40‰ in weight, and/or Zinc in the amount lower than 40‰ in weight or Silver and Zinc the sum of respective amounts in weight is lower than 40‰.

[0112] Alloys according to the above mentioned general formulation, in particular, have a color that, on the CIELAB1976 color chart, shows a coordinate a* comprised in the range [6.5 - 9.5] and a coordinate b* <13.5, preferably comprised in the range [10 - 13.5].

[0113] In alloys according to the above mentioned general formulation, the absence of Vanadium makes it possible to avoid the creation of carbides and oxides; preferably but non-limiting, the alloy according to the invention is also free from Magnesium, Silicon, Titanium, Tungsten, Molybdenum, Niobium, Tantalum, Zirconium, Yttrium, Germanium, and is also free from Nickel, Arsenic and Cobalt. Thanks to this last aspect, the alloy is a Gold alloy compatible with being worn or wearable by subjects whose allergic tolerance is significantly low.

[0114] Without prejudice to the exclusion of unintended impurities, alloys according to the invention can comprise additional materials in total amount, i.e. in sum, not higher than 2‰ and more preferably not higher than 1‰; the list of said additional materials comprises Iridium, Indium, Ruthenium and Rhenium. These materials can have, under certain conditions better explained hereinafter, grain refining properties.

[0115] In particular, Iridium is preferably used in alloys containing high Copper contents, because it binds in particular with the latter element; preferably, but non-limiting thereto, if present, Iridium is present in a maximum amount equal to 0.5‰ in weight. Rarer is the use of Ruthenium and Rhenium, in a sometimes lower amount, but anyway up to 0.5 ‰ in weight. Ruthenium and Rhenium are preferably used in Gold alloys containing Palladium.

[0116] However, it is noted that the use of Iridium or Rhenium and Ruthenium is subject to the inclusion of these elements in pre-alloys. In fact, it has been observed that these elements, if not pre-bonded with the material with affinity thereto, but directly introduced into the pot, do not form alloy, thus contributing to a worsening of the characteristics of the alloy. On the other hand, only if used in pre-alloy with Copper (Iridium) or Palladium (Rhenium and Ruthenium), taking care to make the pre-alloy bind with the rest of the elements composing the alloy itself, it is possible to refine the grain.

[0117] It is also object of the invention a process of production of a Gold alloy, in particular a Gold alloy for jewelry, comprising Gold, Copper, Palladium and optionally Iron according to the above description. The Gold alloys object of the invention are made from pure elements, in particular from Gold at 99.99%, Cu at 99.99%, Pd at 99.95%, Fe al 99.99%, Ag at 99.99%.

[0118] The process of melting of pure elements for the creation of the Gold alloys according to the invention can be in detail a process of discontinuous melting of Gold or a process of continuous melting of Gold. The process of discontinuous melting of Gold is a process in which the mixing is melted and cast into a refractory mold or refractory or metallic ingot mould. In this case the above mentioned elements are melted and cast in a controlled atmosphere. More in particular, the melting operations are carried out only after having preferably conducted at least 3 conditioning cycles of the atmosphere of the melting chamber. This conditioning involves first of all reaching a vacuum level up to pressures lower than $1x10^{-2}$ mbar and a subsequent partial saturation with Argon at 500mbar. During the melting, the Argon pressure is kept at pressure levels between 500mbar and 800mbar. When the complete melting of the pure elements has been reached, a phase of overheating of the mixture takes place, in which the mixture is heated up to a temperature of about 1250°C, and in any case to a temperature above 1200°C, in order to homogenize the chemical composition of the metal bath. During the overheating phase, the pressure value in the melting chamber reaches again a vacuum level lower than $1x10^{-2}$ mbar, useful to eliminate part of the residues produced by the melting of the pure elements.

[0119] At this point, in a casting step, the melted material is casted into a mould or ingot mould realized in graphite and the melting chamber is again pressurized with an inert gas, preferably argon, injected at a pressure lower than 800mbar and in particular lower than 700mbar.

[0120] After solidification, the bars or casts are extracted from the bracket. When the alloy is solidified, from the mold in graphite are obtained Gold bars or Gold alloy casts which are subjected to quick cooling by means of a step of immersion in water, in order to reduce and possibly avoid solid state phase transformations. In other words, the bars or casts are subjected to a quick cooling phase, preferably but non-limiting in water, in order to avoid phase variations in the solid state.

[0121] In a more general embodiment, the production process of the Gold alloy according to the invention comprises, starting from the pure elements according to the above, a mixing step of:

- Gold, in the amount comprised between 540‰ and 620‰ in weight;
- Copper, in the amount comprised between 360‰ and 415‰ in weight;
- Palladium, in the amount comprised between 10‰ and 30‰ in weight;

and a step of introduction of the mixture in a melting pot, and a subsequent melting through heating until melting.

[0122] The process of continuous melting is a process in which solidification and extraction of the solidified Gold are continuously carried out from one free end of a Gold bar or cast. In particular, a graphite die is used in the continuous melting process. The use of graphite dies is known, since graphite is a solid lubricant, and typically has low friction between its surfaces and those of the solidified metal, permitting to obtain an easy extraction of the element contained therein without fractures and with the minimum amount of defects present on its surface.

[0123] When the inclusion of elements such as Iridium, Indium, Ruthenium and Rhenium is present for grain refinement, the production process comprises a step of realizing of a pre-alloy, in which said pre-alloy comprises:

a) Iridium pre-alloyed to Copper in the already indicated amounts, or alternatively
b) Rhenium or Ruthenium pre-alloyed to Palladium in the already indicated amounts.

[0124] Subsequently, the bars or casts obtained by discontinuous or continuous melting are subject to a step of cold plastic deformation, preferably but non-limiting to flat rolling.

[0125] During the flat rolling and more generally during the cold plastic processing steps, the different compositions synthesized according to the previously described melting procedure are deformed by more than 70% and then subjected to a thermal treatment of solubilization at a temperature higher than 680°C, in order to be subsequently cooled.

[0126] Particular embodiments of the previously described method include an initial step in which are mixed in particular Palladium in the amount comprised between 12‰, more preferably 15‰ and 27‰, more preferably 25‰ in weight and/or, in addition to the preceding elements, also Iron comprised between 2‰ in weight and 15‰ in weight, more preferably between 4‰ in weight and 13‰ in weight. In particular, Iron can be comprised between 5‰ and 10‰ in weight. According to a particular embodiment, the method comprises the mixing of Gold, Copper and Palladium such as that the sum in thousandth of their weights is at least equal to 910‰, more preferably 950‰, and even more preferably 960‰ or even 970‰.

[0127] In a particular embodiment of the method of realization of the Gold alloy, the sum of the amounts of Gold, Copper and Palladium is at least equal to 900‰ in weight, and more in particular in the amount at least equal to 960 ‰ in weight, more preferably 970 ‰ in weight. In this case it is possible that the sum of Palladium and Iron is lower than 37‰ in weight, and more preferably lower than 35‰ in weight, wherein Iron is comprised in the amount between 5‰ and 10‰ in weight.

[0128] Another specific embodiment of the method comprises the mixing of Gold in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper between 370‰ and 405‰ in weight and Palladium between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight, or alternatively Gold in the amount comprised between 565‰ and 605‰ in weight, and more preferably between 575‰ and 595‰ in weight, and Copper between 370‰ and 405‰ in weight, with the sum of the amounts of Palladium and Iron comprised between 23‰ and 27‰, even more preferably equal to 25‰.

[0129] With the invention it is then possible to realize a method of production of an item for jewelry or part of an item for jewelry, said method being characterized in that it comprises one or more steps of mechanical processing of a Gold alloy according to the preceding description.

[0130] The advantages offered by the alloy object of the invention are clear in the light of the above obtained description. The alloys are characterized by a low tendency to tarnishing for the environments in which an item of jewelry is typically found to be used, consequently it allows to realize items of jewelry or parts of items for jewelry resistant to tarnishing, in substantially red color as above defined, without the need for subsequent plating with high title Gold alloys. Consequently, the item of jewelry thus created is less expensive and less demanding to be processed as well as characterized by a substantially more uniform color even after wear.

[0131] The alloys according to the present disclosure are alloys without secondary phases. In detail, the alloys according to the present disclosure are homogeneous Gold alloys, free from second phases, and in particular free from carbides and/or oxides and/or are crystalline alloys, in particular 100% crystalline. This permits to have a high strength and quality and surface uniformity. As "free from secondary phases" or "free from second phases" is intended an alloy free from elements that can generate them, in particular in a process of melting and subsequent solidification without other thermal treatments; second phases that create in the liquid phase and remain downstream of the alloy solidification, are harmful second phases, for example carbides and/or oxides that during the polishing step are visible at naked eye on the surface of the polished item, and that then prevent to obtain items with high surface quality, compatible with the needs required in the high jewelry field.

[0132] In the here described process of production of the Gold alloy, it is possible to expose the alloy to thermal treatment processes, able to give it a hardening, so that due to precipitation can be present subtle precipitates, results of said thermal treatment; in this case these are precipitates that prevent from the movement of displacement by increasing the mechanical properties in the material, and withstand the incidence of deformations in the items realized with the present alloys.

[0133] Finally, it is clear that the object of the present invention may be subject to modifications, additions or variants, which are obvious to an expert in the art, without thereby falling outside of the scope of protection provided by the attached claims.

Claims

1. An alloy, in particular for jewelry, **characterized in that** it consists of:

   - Gold, in the amount comprised between 540‰ and 620‰ in weight;
   - Copper, in the amount comprised between 360‰ and 415‰ in weight;
   - Palladium, in the amount comprised between 10‰ and 30‰ in weight;

   and, optionally, at least one among Silver in the amount lower than or equal to 80‰ in weight, Zinc in the amount lower than or equal to 80‰ in weight, Indium in the amount lower than or equal to 20‰ in weight, Tin in the amount lower than or equal to 20‰ in weight, Iron in the amount lower than or equal to 15‰ in weight, Gallium in the amount lower than or equal to 10‰ in weight, Iridium or Ruthenium in the amount lower than or equal to 0.5‰ in weight, Rhenium in the amount lower than or equal to 0.1‰ in weight.

2. Alloy according to claim 1, **characterized in that** it comprises a "pearly red" color and/or **in that** it comprises a color that, on the CIELAB1976 color chart, has a coordinate a* comprised in the range [6.5 - 9.5] and a coordinate b*<13.5, preferably comprised in the range [10 - 13.5].

3. Alloy according to any of the preceding claims, **characterized in that** it comprises Palladium in the amount comprised between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight.

4. Alloy according to any of the preceding claims, **characterized in that** it comprises also Iron in the amount comprised between 2‰ in weight and 15‰ in weight, more preferably between 4‰ in weight and 13‰ in weight, even more preferably between 5‰ and 10‰ in weight and/or **in that** the sum of the amounts of Gold, Copper and Palladium is at least equal to 910‰ in weight, more preferably 950‰ in weight, even more preferably 960‰ in weight, and even more preferably 970‰ in weight.

5. Alloy according to claim 4, **characterized in that** the sum of the amounts of Palladium and Iron is equal to or lower than 37‰ in weight, and more preferably lower than 35‰ in weight and **in that** Iron is comprised in the amount between 5‰ and 10‰.

6. Alloy according to any of the preceding claims, wherein Gold is present in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight, and Palladium is comprised between 12‰, more preferably between 15‰ in weight, and 27‰, more preferably 25‰ in weight.

7. Alloy according to claim 4 or claim 5, **characterized in that** Gold is present in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and the sum of Palladium and Iron is comprised between 23‰ and 27‰, even more preferably substantially equal to 25‰.

8. Alloy according to claim 5, **characterized in that** it comprises Palladium in the amount comprised between 13‰ in weight and 17‰ in weight, preferably between 14‰ in weight and 16‰ in weight and even more preferably in the amount substantially equal to 15‰ in weight.

9. Alloy according to claim 4 or claim 5, **characterized in that** Gold is present in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper is present between 370‰ and 405‰ in weight and the sum of Palladium and Iron is comprised between 30‰ and 35‰.

10. Alloy according to any of the preceding claims, **characterized by** the absence of Vanadium and other materials capable to create carbides and oxides, in particular free from Magnesium, Silicon, Titanium, Tungsten, Molybdenum, Niobium, Tantalum, Zirconium, Yttrium, Germanium and/or in that it is free from Nickel, Arsenic and Cobalt.

11. A method of production of a Gold alloy; said method being **characterized in that** it comprises:

a) a step of homogenization wherein all the pure elements constituting the alloy are melted in such a way as to obtain an homogeneous solution or mixture; this mixture comprises in weight at least:

- Gold, in the amount comprised between 540‰ and 620‰ in weight;
- Copper, in the amount comprised between 360‰ and 415‰ in weight;
- Palladium, in the amount comprised between 10‰ and 30‰ in weight;

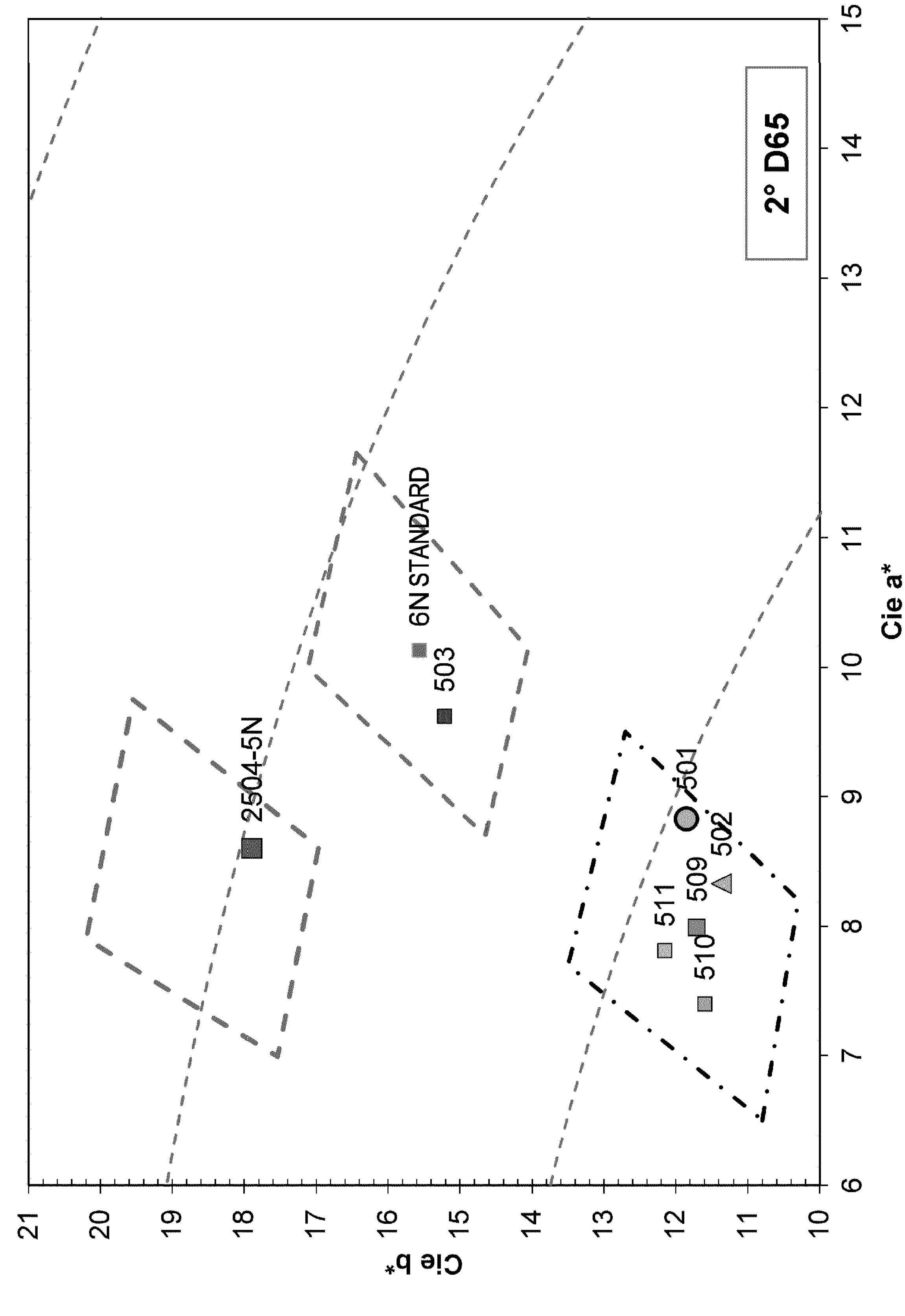
for creating a mixture; and
b) a step of introduction of the mixture in a melting pot, and a subsequent melting through heating until melting.

12. Method according to claim 11, wherein said step of homogenization comprises mixing in particular Palladium in the amount comprised between 12‰, more preferably 15‰ in weight, and 27‰, more preferably 25‰ in weight.

13. Method according to claim 11 or 12, comprising the mixing of, in addition to the preceding elements, also Iron in the amount comprised between 2‰ and 15‰ in weight, more preferably between 4‰ and 13‰ in weight, even more preferably between 5‰ and 10‰ in weight, optionally such that the sum of the amounts of Gold, Copper and Palladium is at least equal to 910‰ in weight and preferably in the amount at least equal to 950 ‰ in weight, more preferably 960‰ in weight.

14. Method according to claim 13, comprising the mixing of Gold in the amount comprised between 565‰ in weight and 605‰ in weight, and more preferably between 575‰ in weight and 595‰ in weight, and Copper in the amount comprised between 370‰ and 405‰ in weight, and Palladium in the amount comprised between 12‰, more preferably between 15‰ in weight, and 27‰, more preferably 25‰ in weight.

15. Item of jewelry, at least partially realized through a Gold alloy according to one or more of claims 1 to 10.


2° D65
Cie b*
Cie a*
2504-5N
6N STANDARD
503
501
502
509
510
511
21
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19
18
17
16
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FIG.1

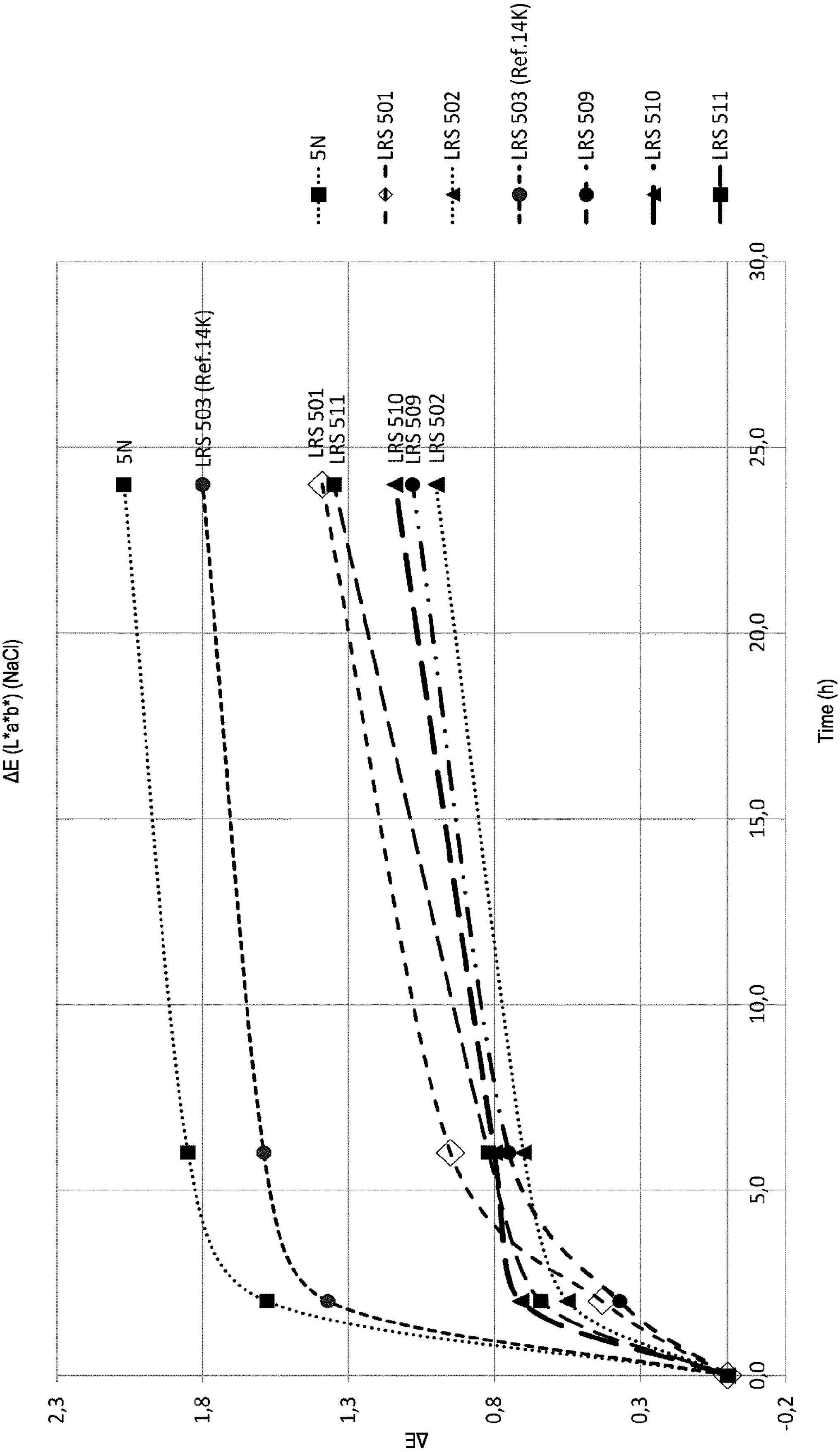
ΔE (L*a*b*) (NaCl)
ΔE
Time (h)
2,3
1,8
1,3
0,8
0,3
-0,2
0,0
5,0
10,0
15,0
20,0
25,0
30,0
5N
LRS 503 (Ref.14K)
LRS 501
LRS 511
LRS 510
LRS 509
LRS 502
5N
LRS 501
LRS 502
LRS 503 (Ref.14K)
LRS 509
LRS 510
LRS 511

FIG.2

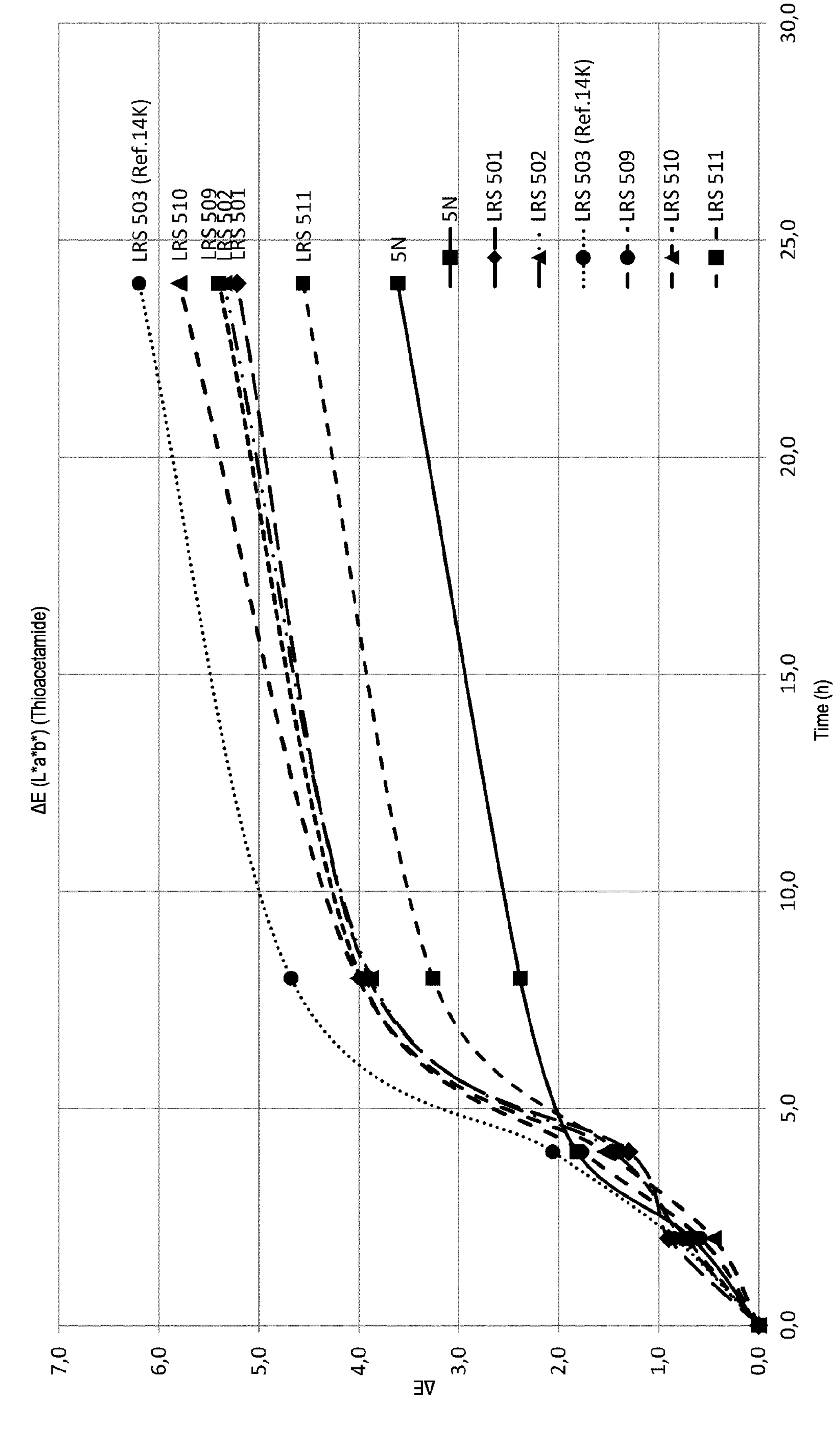
ΔE (L*a*b*) (Thioacetamide)
ΔE
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0,0
5,0
10,0
15,0
20,0
25,0
30,0
Time (h)
LRS 503 (Ref.14K)
LRS 510
LRS 509
LRS 502
LRS 501
LRS 511
5N
5N
LRS 501
LRS 502
LRS 503 (Ref.14K)
LRS 509
LRS 510
LRS 511

FIG.3

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EUROPEAN SEARCH REPORT

Application Number
EP 19 16 9009

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 5 340 529 A (DEWITT TROY C [US] ET AL) 23 August 1994 (1994-08-23) * abstract * * column 2, line 50 - line 54 * * column 3, line 58 - column 4, line 2 * * column 4, line 16 - line 17 * * column 4, line 25 - line 27 * -----	1-15	INV. C22C5/02 A44C27/00 ADD. C22F1/14
A	WO 2014/087216 A1 (ARGOR HERAEUS SA [CH]) 12 June 2014 (2014-06-12) * abstract * -----	1-15	
A	GB 2 245 590 A (AGENCY IND SCIENCE TECHN [JP]; SEKI KK [JP]) 8 January 1992 (1992-01-08) * abstract * -----	1-15	
A	ALLEN S MCDONALD ET AL: "The metallurgy of some carat gold jewellery alloys", GOLD BULLETIN, vol. 11, no. 3, 30 September 1978 (1978-09-30), pages 66-73, XP055497232, London, UK ISSN: 0017-1557, DOI: 10.1007/BF03215089 * abstract * -----	1-15	TECHNICAL FIELDS SEARCHED (IPC) C22C A44C C22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	5 July 2019	Rosciano, Fabio

CATEGORY OF CITED DOCUMENTS

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