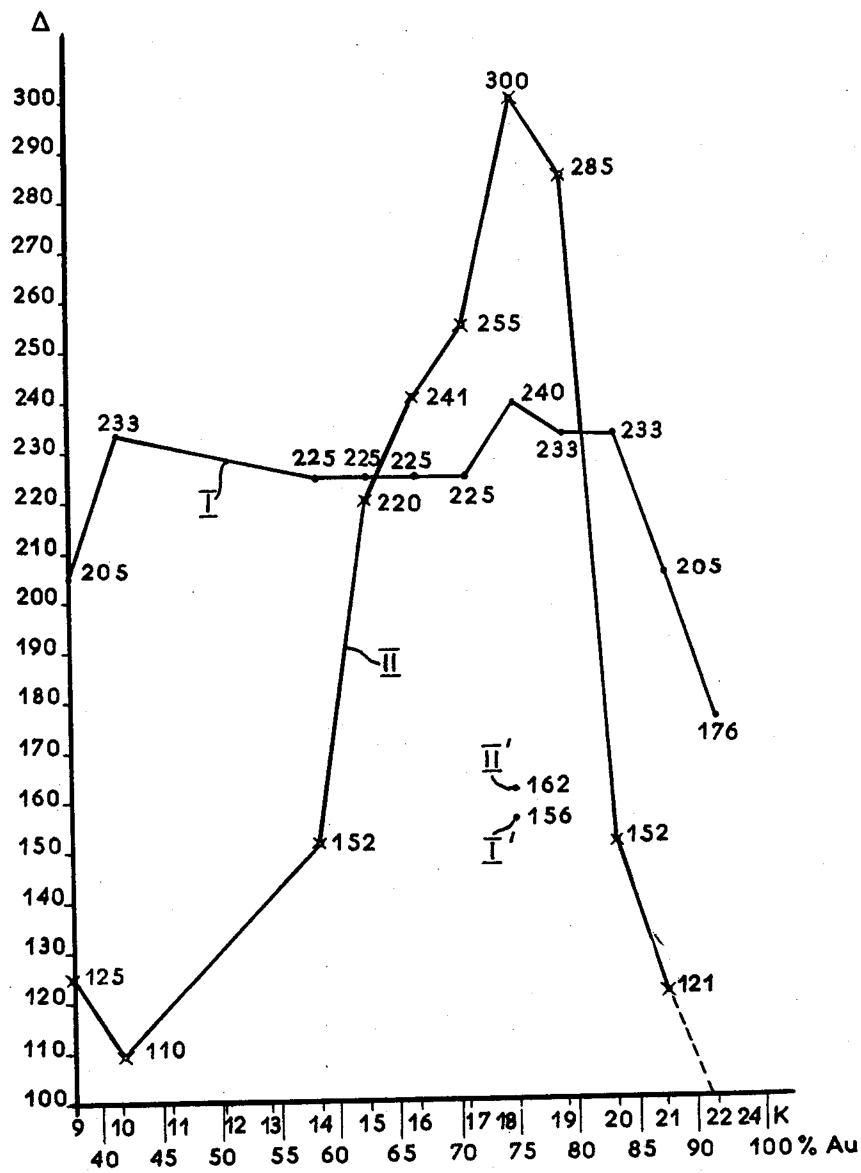
July 21, 1964 E. BRELLIER ETAL 3,141,799

HEAT TREATMENT OF GOLD ALLOYS

Filed Aug. 27, 1958



United States Patent Office

3,141,799
Patented July 21, 1964

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3,141,799
HEAT TREATMENT OF GOLD ALLOYS

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Filed Aug. 27, 1958, Ser. No. 757,593
6 Claims. (Cl. 148—11.5)

This invention relates to gold alloys and their heat-treatment.

An object of the invention is a range of gold alloys which after an appropriate heat-treatment can acquire very superior mechanical, physical (including electrical) or/and chemical properties.

Various gold alloys have been proposed having particular mechanical, physical and chemical properties, such as high resistance to oxidation, hardness or/and rigidity, e.g., for the nibs of fountain pens, jewellery, watch cases or dentures and tooth-fillings.

A further object of the invention is a range of gold alloys, which while having high resistance to oxidation by normally encountered corrosive agents, become, after an appropriate heat-treatment, either softer (more malleable or ductile) or harder and more elastic than conventional gold alloys, or again are substantially insensitive to heat treatment according to their original composition and more especially their gold content, and which in some cases can acquire an exceptionally high degree polish of optical quality.

The alloys comprised in the objects of this invention are all characterized by a content of copper, nickel and zinc and optionally a small amount of manganese, the ranges of the three principal alloying constituents, expressed as percentages by weight of the whole content of alloying constituents, i.e., other than the gold itself, being as under:

	Percent
Cu	65 to 90
Ni	4 to 25
Zn	3 to 10

the manganese content, if present, being of the order of 0.1% by weight of the whole content of the alloying constituents, not including the gold.

Thus, if for instance the gold content of the alloy were 50% by weight, the ranges by weight of the contents of copper, nickel and zinc in the whole alloy, including the gold, would be

	Percent
Cu	32.5 to 45
Ni	2 to 12.5
Zn	1.5 to 5

and correspondingly for different values of the gold content, which normally may lie within the range 9 to 22 carats, i.e., 37.5% to 92% by weight.

Within the above defined range of gold content of an alloy as above described, different properties result from a heat-treatment consisting of rapid quenching to ambient temperature from an elevated temperature, below the alloy's melting point, followed by re-heating to a lower temperature (than said elevated temperature) and natural cooling either with or without more or less prolonged soaking (for at least an hour) at such lower temperature, as follows: if the gold content (by weight) is less than 60% or more than 80%, the heat-treatment softens the alloy; but if the gold content is between the above values of 60% and 80%, the heat-treatment hardens it and makes it more elastic. If, however, the gold content is substantially 60% or 80% by weight, the alloy is substantially insensitive to the above-mentioned or to any heat-treatment.

Alloys in accordance with the invention whose gold

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content lies between 60% and 80% by weight are especially suitable for articles requiring cold-(or hot-)working, e.g., rolling, wire-drawing or stamping. Naturally such operations will be performed before the heat-treatment which confers hardness and elasticity.

Industrial applications for which alloys comprised within the scope of this invention are especially suitable include—the electronic art, jewellery and dental applications. Of such alloys can be made springs and contacts of high mechanical strength and resilience, articles having high resistance to shock, corrosion and wear, as well as composite articles including different portions made respectively of a soft alloy and a hard alloy, such composite articles being especially useful in dental applications.

Yet another object of the invention is the above described method of heat-treating gold alloys having the compositions hereinbefore defined.

The nature of the invention, its objects and how it may be carried into practice will be more readily understood from the following detailed description, given by way of example only and without implied limitation of the scope of the invention as defined in the hereto appended claims, such description referring to specific examples of practice and illustrated by the graph shown in the accompanying single figure of drawings, in which "Brinell" hardness (Δ) is plotted as ordinates against gold content, measured both in carats (K) and in percentages by weight, as abscissae.

In the drawing, curves I and II are representative of alloys in accordance with the invention as hereinbefore defined, curve I relating to the initial "as forged (or hammered)" state and curve II to the state after subsequent heat-treatment consisting of:

Preliminary annealing for four hours at 300° C.;
Heating in a reducing atmosphere to 700° C.;
Soaking in the same atmosphere and at the same temperature for one hour;
Rapid quenching in liquid, e.g., alcohol, at ambient temperature;
Re-heating to 250° C.;
Soaking at the latter temperature for one hour; and
Natural cooling to ambient temperature.

Points I' and II' relate to a conventional similarly pink coloured gold alloy of 18 carats, point I' referring to the "as forged" state and point II' to the state after a subsequent heat-treatment as defined above for curve II.

The graph shows that if the gold content of an alloy according to this invention is in the neighbourhood of 60% or 80% the heat-treatment has very little effect on its hardness; but if the gold content is substantially below 60% or substantially above 80% the heat-treatment brings about a startling reduction of hardness, whereas if the gold content is within the range 60% to 80% the heat-treatment increases the hardness, the peak hardness occurring at a gold content in the neighbourhood of 75%=18 carats. The alloy of this gold content has an elasticity comparable to that of spring steel. The peak hardness figure of 300 degrees Brinell is nearly twice that of the 18 carat conventional pink alloy, represented by points I' and II' which is little affected by heat-treatment.

One specific example of an 18 carat alloy according to the invention (hereinafter referred to for brevity as "the specific alloy") has the following constitution:

	Percent by weight
Au	74.5±0.2
Cu	21.7±0.2
Ni	2.48±0.05
Zn	0.9±0.05
Mn	0.02±0.005

This composition is determined analytically, the dosage of gold being effected in the metallic state, that of copper being determined by electrolysis, that of nickel by dimethylglyoxide, that of zinc in the oxide state and that of manganese by colorimetry.

A sample of this composition, assaying 18 carats, was melted in a high-frequency furnace under an atmosphere of nitrogen. Temperatures were plotted against time by means of an electronic potentiometer connected to a "chrome-Alumel" thermocouple whose hot junction was immersed in the crucible. The steps of melting and solidification were repeated three times in succession and substantially identical temperature-time curves were obtained each time showing a solidification point of approximately 899° C.

X-ray examination carried out on a wire of the specific alloy, shows that its crystal structure in the cold-worked state is a face-centered cube whose parameter a is approximately 3.86×10^{-8} cm. showing it to be comparable with gold whose crystal is a face-centered cube having a parameter a of 4.07×10^{-8} cm. approximately.

The electrical resistivity ρ of the specific alloy at 20° C. in the cold-worked state is 20.2 $\mu\Omega$/cm. (or say 20 $\mu\Omega$/cm.) and in the heat-treated state (heat-treatment as described above) is 19.6 $\mu\Omega$/cm. (or say 19 $\mu\Omega$/cm.). For comparison the resistivity of pure gold is about 2 $\mu\Omega$/cm. and that of an 18 carat gold-silver pink alloy about 8 $\mu\Omega$/cm. These resistivity characteristics of the specific alloy are especially valuable in electronic applications.

Tensile testing has been carried out, on an "Amsler" type machine, of a test piece of the specific alloy having the following dimensions, after rapid quenching from about 700° C. followed by reheating to and soaking for one hour at about 200° C., length of calibrated portion 60 mm., width 10.1 mm. and thickness 1.02 mm. The cross-sectional area, "S′," is therefore 10.3 mm.² and the length, "L" ($=8.16\sqrt{S}$) on which elongation is computed is 26 mm.

The results of this test are as follows:

Elastic limit	kg./mm.²	77.5
Ultimate tensile stress	kg./mm.²	96
Elongation (at rupture)	percent	5

Hardness tests, on a test piece, 1.2 mm. thick, of the same alloy, before and after the described heat-treatment, done on a "Vickers-Amsler" type machine, with 10 kg. load, and measured on the scale 10 have given the results set out in the following Table I (setting out the results of a number of experiments).

Table I

2 mm. test pieces:	Vickers hardness, scale 10
Initial state	230, 235, 235, 240, 232
After cold-working (rolling)	270
After subsequent quenching from 700° C.	143, 145, 149, 149, 144
After subsequent re-heating to and soaking for one hour at 200° C.	247, 260, 247, 254
After further re-heating to 260° C.	220, 220, 229, 208, 211
1 mm. test pieces: After quenching from 700° C. and re-heating to, with soaking for one hour at 200° C.	292, 274, 285, 285, 283.

For comparison, the hardness of a conventional 18 carat gold, measured on the same scale, is from 120 to 160 (Vickers) units and is substantially insensitive to heat-treatment.

Further heat-treatment experiments carried out, with different quenching and re-heat temperatures and different re-heat soaking times, on the same (specific) alloy, both as made freshly, without preliminary working and as made by remelting, with inclusion of more or less scrap from previously worked articles (of the same composition) have given results as set out in Table II.

Table II

Test No.	Origin of Alloy	Quenching Temperature (° C.)	Re-heat Temperature (° C.)	Re-heat Soaking time (Hrs.)	Vickers Hardness
1	Fresh	500	None	None	185
2	do	500	100	4	180
3	do	700	300	1	296 to 300
4	do	700	300	1	285 to 292
5	do	700	350	1½	180 to 190
6	do	700	350	1	300
7	do	880 to 890	None	None	160
8 Remelt (including a proportion of scrap).	do	700	250	1	284
9	do	700	300	1	223
10	do	700	300	1	220 to 240
11	do	700	350	1½	175
12	do	700	350	1	155

This "specific" 18 carat alloy has superior elastic properties approaching those of tempered steel. Its colour is much the same as that of a conventional pink coloured gold (having a content of copper and silver) and it has a better brightness and resistance to oxidation. Moreover, it does not blacken the skin; and is easier to roll and wire-draw. Thus an ingot of it about 4 mm. thick, 3 cm. wide and 7 to 8 cm. long, as delivered from ingot mould, can be rolled down to a thickness of about 0.2 mm. without having to be re-heated and without fracture. It is well suited for making "doubled" or "laminated" articles or pieces, e.g., having a silver basis plated (or interleaved with) the "specific" gold alloy. Such a "doubled" piece can be embossed with uniform thicknes without tearing and articles so fabricated do not tarnish or blacken the skin. For soldering an 18 carat alloy according to the invention, such as the specific alloy above defined, a conventional 18 carat gold alloy can be used, since the melting point of the latter is about 100° C. below that of the former.

Threads of conventional 18 carat gold will usually break when wound (on a bobbin or the like) unless re-heated after drawing, but threads of an alloy according to this invention are not subject to this defect. Soldered springs, of especial utility in electronic applications, can be successfully made of alloys according to this invention.

Pieces of 18 carat alloy, of constitution and heat-treated in accordance with this invention, take a higher polish and are less easily scratched than conventional 18 carat gold pieces.

Alloys in accordance with this invention can be prepared without much difficulty. Crucibles or refractory material or conventional graphite can be used, heated in any convenient way, e.g., by a gas or compressed air blow-pipe of the "Mecker" type, or by an induction furnace.

By the way of example, the following procedure may be adopted:

A "primary" alloy, comprising all the constituents, other than gold, of the ultimate alloy in the prescribed proportions, is first prepared as follows:

A pinch of borax (which facilitates the subsequent operations) is placed in a graphite crucible of suitable size. The nickel is then introduced and the crucible is heated to the melting point of nickel. Next, the copper is added, while maintaining the heating, the contents being agitated with a graphite stirrer until the copper is dissolved. The zinc is then added and (contingently) the manganese. When all these metals are completely melted and thoroughly mixed, the "primary" alloy thus formed is granulated by quenching in water at ambient temperature.

It may here be mentioned that instead of introducing the copper and zinc separately, a brass of the appropriate composition may be used; this accelerates the melting and makes it more uniform.

The next step is to place an appropriate amount of the granulated primary alloy, with a pinch of borax, in the bottom of a crucible of refractory material and to cover it with the appropriate quantity (having regard to the ultimate gold content required) of fine gold. The crucible is then heated, while its contents are agitated with a graphite stirrer, until the contents melt. When the contents have been thoroughly homogenised, the resultant homogenised alloy is poured into ingot moulds and the ingots so produced are cold-(or hot-)worked in the conventional way.

Heat-treatment as hereinbefore defined is then applied. The preliminary preparation of a "primary" alloy of metals other than gold enables the "dosage" of gold to complete the ultimate alloy to be more precisely controlled. The procedure described above is also advantageous in that the gold, being introduced into the crucible on top of the primary alloy, to some extent protects the metals of the latter from oxidation when fusion starts.

The above-described method of preparing an 18 carat gold alloy, according to this invention, is applicable, mutatis mutandis, to the preparation of similar alloys assaying different gold contents.

Again, all the constituents of the ultimate alloy, including the gold, may be mixed in a single initial melt.

Alloys according to this invention having a gold content between about 60% and 80% have properties to some extent comparable with those of beryllium bronzes, which are characterized by the peculiarity of being softer in the quenched or tempered state than in the "as forged" state, the reverse being the case with most of the usual industrial metals and their alloys.

The alloys according to the invention may include other constituents than those specifically mentioned, albeit in somewhat small proportions; and other constituents may be introduced in the course of fabrication, to be ultimately removed, with a view to facilitating homogenization, fusion or/and alloying. In this connection, the introduction of cadmium, to be removed, at least partially, from the final product, may in some cases be useful.

Although the foregoing detailed description refers mainly to an 18 carat gold alloy having specific contents of copper, nickel, zinc and manganese, and to a specific preferred method of making and heat-treating it, the principles described can be applied, with such modifications and variations of composition and treatment, within the scope of the invention as defined in the hereto appended claims as are appropriate and are within the competence of those skilled in the art, to the making of alloys assaying different gold contents or/and having different proportions of alloying elements, and to their subsequent treatment.

What is claimed is:

1. A method of producing a gold alloy having a selected hardness, comprising the steps of providing an alloying composition of 65% to 90% (by weight) copper, 4% to 25% (by weight) nickel and 3% to 10% (by weight) zinc; melting said alloying composition with an amount of gold comprised between about 37.5% and 92% relative to the total weight of said gold alloy, until a homogeneous gold alloy is obtained; cooling said alloy to ambient temperature; working said alloy by submitting it to plastic deformation; and submitting said alloy to a heat treatment comprising the steps of heating the alloy to an elevated temperature lower than the melting point of the alloy; rapidly quenching the alloy at ambient temperature; reheating the alloy to a temperature substantially lower than said elevated temperature; and cooling the alloy naturally to ambient temperature, said alloy having a Brinell hardness which increases from about 110 degrees to about 300 degrees as the gold content of the alloy increases from about 10 carat to about 18 carat,

while said Brinell hardness decreases from about 300 degrees to about 121 degrees as said gold content increases from about 18 carat to about 21 carat.

2. A method according to claim 1, wherein said alloying composition further includes an amount of manganese comprised between 0.005% and 0.025% of the total weight of said gold alloy.

3. A method according to claim 1, wherein said amount of gold is substantially 60% of the total weight of said gold alloy, the latter being substantially insensitive to heat treatment.

4. A method according to claim 1, wherein said amount of gold is substantially 80% of the total weight of said gold alloy, the latter being substantially insensitive to heat treatment.

5. A method according to claim 1 for producing an 18 carat gold alloy, wherein said alloy contains 21.7%±0.2% copper, 2.48%±0.05% nickel, 0.9%±0.05% zinc, said alloy further including 0.02%±0.005% manganese of the total weight of said gold alloy, the latter having a Brinell hardness of about 300 degrees.

6. A method of producing a gold alloy having a selected hardness, comprising the steps of providing an alloying composition consisting of 65% to 90% (by weight) copper, 4% to 25% (by weight) nickel and 3% to 10% (by weight) zinc, said composition being prepared by first melting the nickel, then adding the copper to the molten nickel, melting the copper, adding the zinc to the molten nickel and copper, melting the zinc, and thereafter granulating said alloying composition by quenching it in water at ambient temperature; melting said alloying composition; adding to the molten alloying composition an amount of gold comprised between about 37.5% and 92% relative to the total weight of the gold alloy; melting said gold in said molten alloying composition to produce a homogeneous ally consisting of said gold, copper, nickel and zinc; cooling said alloy to ambient temperature, working the alloy by submitting it to plastic deformation; submitting the alloy to a heat treatment comprising the steps of preliminarily heating the alloy for about 4 hours at about 300° C.; heating the alloy to about 700° C. and soaking it for about one hour at about 700° C. in a reducing atmosphere; quenching the alloy in a liquid at ambient temperature; heating the alloy to about 250° C. and soaking it for about one hour at about 250° C.; and naturally cooling the alloy to ambient temperature; said alloy having a Brinell hardness which increases from about 110 degrees to about 300 degrees as the gold content of the alloy increases from about 10 carat to about 18 carat, while said Brinell hardness decreases from about 300 degrees to about 121 degrees as said gold content increases from about 18 carat to about 21 carat.

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