Hardenable 22 carats gold alloys

1. Introduction

22K gold alloys are not prone to hardening by means of the commonly used components (such as silver, copper, zinc, nickel), while they are by the use of cobalt (with quantities above 15‰).
On the other hand, the use of cobalt is restricted to the fact that this element can only be partially introduced in the alloy as master alloy (Cu/Co 950/50 or 900/100‰), since the maximum introducible quantity does not allow the obtainment of the necessary conditions for hardening — e.g. in a 22K alloy, which thus contains 917‰ gold, you can introduce a cobalt quantity of 8.3‰ only, with the Cu/Co 900/100 alloy. This without getting to the heart of the matter of an alloy containing gold, copper and cobalt only.

In conclusion, to obtain a product with such minimum cobalt quantity to make it hardenable, cobalt has to be directly introduced in the alloy when casting gold with the master alloy; then, it is clear that the burden of result is left to the ability of the alloy producer, since cobalt produces a high superficial oxidation, in addition to being notably difficult to cast[1].

The possibility of hardening 22K gold alloys starting from a master alloy is a very important goal and still not reached. This paper is aimed to describe the proceeding used for developing a master alloy which, alloyed with gold in 917‰, is able to supply, after proper heat treatment, a hardness equal to that of a 18K yellow gold after casting. The purpose of our job was to obtain a hardenable 22K alloy, so we made hardness and crystalline grain measurements only. This means that this was a practical work, that is we looked for the results first and then the complete characterization would be carried out (we are currently doing it).

2. Experimental part

Pure gold is commonly known as soft and ductile. High gold content alloys (such as 22K alloys) are extremely soft as well, as the restricted quantity of alloy does not allow the obtainment of an acceptable hardness.

We carried out a preliminary bibliographic research, discovering that a higher hardness is looked for by means of a microalloying of elements such as titanium, calcium, beryllium, gallium, erbium, or by lanthanoids[2]. From what found in bibliography, a hardenable alloy does not exist, if not with a notable cobalt quantity, with all those problems this element involves — it is toxic, easily oxidizable, it requires much attention for the obtainment of investment cast items. Then, considered the scarcity of news about and the restricted experience for the 22K, we produced a series of samples to verify what reported in bibliography. We did not take into consideration the hardening obtainable by a solid solution with microalloying of different oxides or by inserting rare earts. Table 1 shows the compositions of the first alloys we tested.

Table 1 – Tested compositions [‰]

Alloy	Au	Ag	Zn	Cu	Co	Ir
1-Ag10Zn10	917	10	10	63	-	-
2-Ag20Zn3	917	20	3	60	-	-
3-Ag40Zn6	917	40	6	37	-	-
4-Ag60Zn10	917	60	10	13	-	-
5-Ag40Zn6Ir	917	40	6	36,85	-	0,15
6-Ag20Zn3Co3	917	20	3	57	3	-
7-Ag37Zn6Co2	917	37	6	38	2	-
8-Ag37Zn6Co1,6Ir	917	37	6	38,22	1,63	0,15
9-Zn41Co1,7Ir	917	-	41,6	39,65	1,7	0,15
10-Ag37Zn6Co20	917	37	6	20	20	0

We tested these compositions to check the possibility of hardening 22K gold alloys starting from common quaternary alloys. In the first four alloys we changed the quantity of silver and zinc (and, consequently, the copper quantity) to check if a copper-silver ratio which might increase hardness exists. We added a grain refiner to the fifth alloy, to verify a possible interaction with the reachable hardnesses. From the sixth to the ninth alloy we introduced small quantities of cobalt (by means of a Cu/co 950/50 alloy), to check if we could increase the hardness with a limited cobalt quantity. In particular, we inserted the maximum possible cobalt quantity using the Cu/Co alloy cited above. Alloys 8 and 9 were used to verify the possible interaction between iridium and cobalt. The last alloy was cast to verify if a hardness increase could occur with cobalt percentages above 15‰, by inserting pure cobalt instead of the Cu/Co alloy.

We cast 100g for each alloy and we poured in a 8mm thickness mold. We rolled the so-obtained ingot up to a 2mm thickness — so, applying a deformation of 75%. We cut different sheets (sized 16x8mm) and we annealed them at different temperatures. The sheets of these first alloys were annealed for 18 minutes at following temperatures: 450, 500, 550, 600, 650, 700, 750°C. Then we carried out a hardness test and an observation of the grain size to determine the most suitable annealing temperature. Figures 1-2 show an example of the values measured for Alloy 3 (Ag40-Zn6). We took Alloy 3 as sample because it has average values for silver and zinc as regards the other compositions and we did not report the values of all the Alloys because this is not the purpose of our paper.

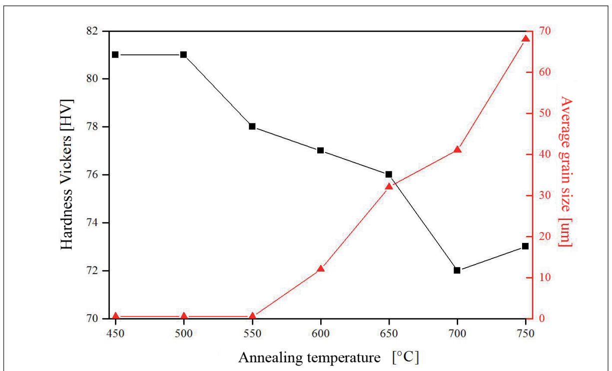

Figure 1 – Average hardness and grain size values of Alloy 3 (Ag40Zn6) at different annealing temperatures

In this way we could determine the suitable annealing temperature, that is 700°C for all the tested Alloys.
We also verified the annealing temperature by the TG/DTA[3], which confirmed the result obtained by grain and hardness. Once verified that even in 22K the right annealing temperature could be determined by TG/DTA, we decided that the temperatures of all Alloys would be determined by TG/DTA exclusively.

We hardened these first ten Alloys for 180 minutes at 250, 300, 400 and 500°C, to check the temperature able to supply the higher hardness. Obviously, the heat treatments were carried out in a furnace under protective atmosphere (argon was used as protective gas). Figure 2 shows the hardness values found out in different conditions.

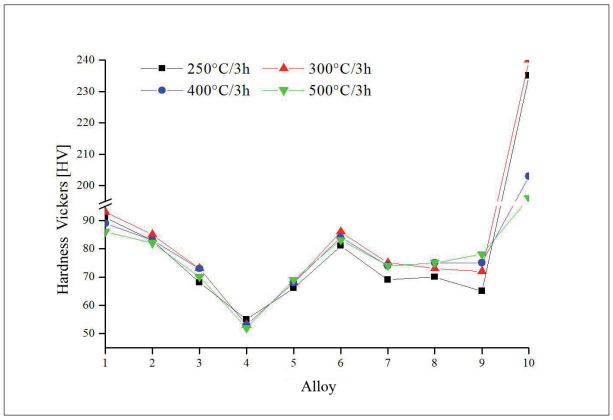

Figure 2 – Hardness values measured after hardening for 180 minutes at different temperatures

From this graph you can notice that the first four alloys displayed a reduction of hardness, according to the trend of the copper quantity contained in the alloy. In particular, the higher the copper quantity was, the higher the hardness of the alloy was. On the contrary, different quantities of silver and zinc did not influence hardness, except for the fact that they limited the quantity of copper present in the alloy. The introduction of iridium in Alloy 5 had only the effect of refining the grain: the measured hardness values corresponded to those of Alloy 3, which had the same composition but without iridium. Small cobalt additions did not alter hardness; in fact the measured hardness values of Alloys 6-9 corresponded to the hardness reached by the Alloys with the same copper quantity (the hardness peak) of Alloy 6 corresponded to the hardness of Alloy 2, which contained a similar copper quantity. Neither the interaction between iridium and cobalt had any effect on the final hardness. Alloy 10, with high cobalt content, reached 250HV, and confirmed what found in literature.

In conclusion, he hypothesized that the hardness reached by the first 9 Alloys was function of the quantity of ordered structure which shaped in the alloy (it was function of the copper quantity, considered that gold was even exceeding, and from the binary phase diagrams it was supposed to be the CuAu3 super-lattice)[4]. As for Alloy 10, the hardness increase was probably due to the precipitation of particles scattered in the alloy (this phenomenon is commonly known as precipitation hardening or age hardening).

Excluding the use of cobalt, we carried on another bibliographic investigation, searching for alloys able to give ordered super-structures. We found interesting the following alloys: Au-Cu, Cu-Zn, Ni-Sn, Ni-Ga, Co-Pt[5]. Since we had already verified the Au-Cu results, considered that Cu-Zn in the introduced quantity seemed to not alter the 22K microstructure — see Alloy 9 (Zn41Co1Ir7) — we decided to try the Ni-Sn system.

With the same preparation of the previous Alloys we tested the composition reported on Table 2.

Table 2 – Ni-Sn Compositions [‰]

Alloy	Au	Ag	Zn	Cu	Ni	Sn	Re
11-Ni42Sn13,8Re	917	-	-	23	42	12,8	4,2
12-Ag20Zn3Ni17Sn3Re	917	20	3	39	17,1	3	0,9
13-Ag30Zn10Ni9Sn3Re	917	30	10	30	9,1	3	0,9
14-Ag30Zn10Ni4,5Sn3Re	917	30	10	36,5	4,55	1,5	0,455
15-Ag20Zn3Ni9Sn11Re	917	20	3	39	9,1	11	0,9
16-Ag20Zn3Ni4,5Sn11Re	917	20	3	44	4,55	11	0,455
17-Ag20Zn3Sn11	917	20	3	49	-	11	-
18-Ag30Zn3Ni20	917	30	3	30	20	-	-

First we prepared Alloy 11, with the previously described proceeding. The composition was thought to obtain an alloy saturated of nickel and tin. Besides, we added rhenium as grain refiner.
We had some difficulties in deforming this sample to 75%, it was very hard (small indentations appeared on the side). So, there was either too much nickel, or too much tin or, still, the problem was due to the synergic action of both these elements. The grain of this Alloy is very well refined. You can see some details of this sample in Figures 3-4.

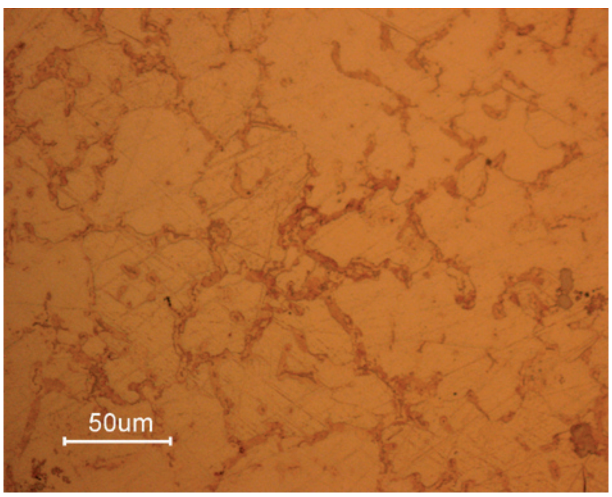

Figure 3 – Grain of Alloy 11 after mold casting

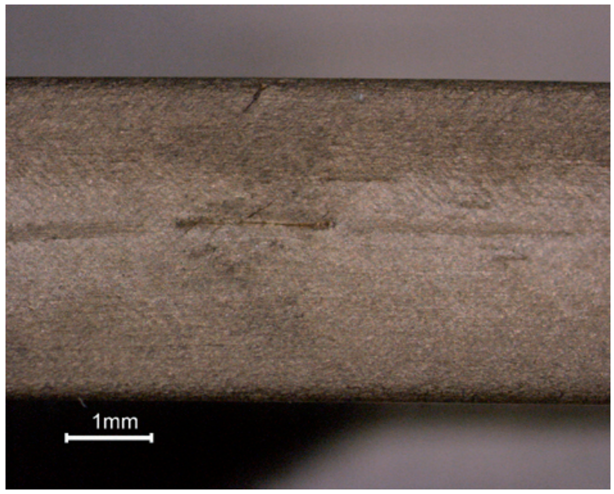

Figure 4 – Side of Alloy 11 after a 60% deformation

This Alloy was annealed at 700°C for 18 minutes, obtaining a hardness value of 134HV. Then it was hardened at 250, 300 and 400°C for 180 minutes (considered the previous Alloys' results we excluded the annealing at 500°C). These tests gave us a maximum hardness value of 264HV, for the hardening at 300°C for 180 minutes. It was evident that too much zinc and tin were inserted, but the important element was the fact that a hardness increase after heat treatment took place. The other Alloys were developed to determine the suitable quantity of nickel and tin able to guarantee acceptable hardnesses. In particular, in Alloy 12 the nickel quantity was cut by half and tin and rhenium were lowered to quantities inferior than a quarter each (seen the phase diagrams we feared the formation of a phase with low melting range due to the tin, while as for rhenium, we noticed that a much inferior quantity was needed). Besides, we added also silver and zinc.
It is to notice that Alloy 11 is white colored, while the aim of this paper is to obtain an alloy for yellow gold, then the nickel quantity has to be reduced. We cut by half the nickel quantity in Alloy 13, without changing tin and grain refiner, but slightly varying silver and zinc quantities. In Alloy 14 we halved nickel, tin and rhenium quantities as regards Alloy 13. The nickel quantity was kept low in Alloys 15 and 16, while tin was notably increased, because we would rather obtain an alloy with the lowest possible content of nickel. Alloys 17 and 18 were developed to check if higher hardness could depend on the only addition of nickel, of on the addition of tin only, or if the contemporaneous presence of both elements was required. Figure 5 shows the trend of hardness for these Alloys, all hardened at 250, 300, 400°C for 180 minutes after an annealing carried out at 700°C for 18 minutes.

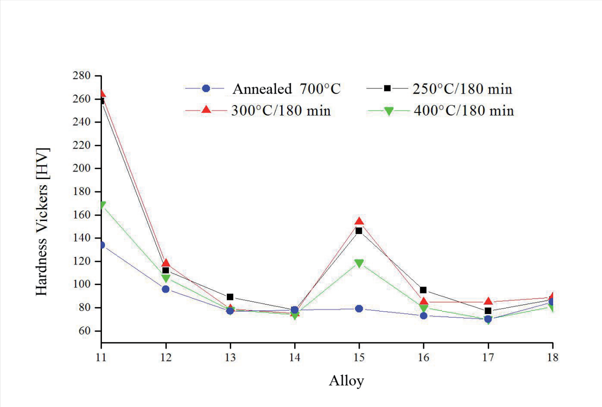

Figure 5 – Hardness values measured after hardening for 180 minutes at different temperatures

In this diagram we reported the values measured after annealing, to try and check the hardening of each alloy. As you can notice, samples which underwent an appreciable hardening contained a minimum quantity of nickel and tin, and the contemporaneous presence of both elements was required. In particular, the alloys with a nickel content lower than 9.1‰ (with contemporaneous presence of tin) did not harden, as samples with a tin content lower than 11‰ (with contemporaneous presence of nickel) did not harden. Probably, the only function of rhenium was to refine the crystalline grain, and it did not interact with the mechanism of hardening. In Figures 6 and 7 you can see the microstructure of Alloy 15 (Ag20Zn3-Ni9Sn11) after mold casting and the rolling side after a reduction of 75%.

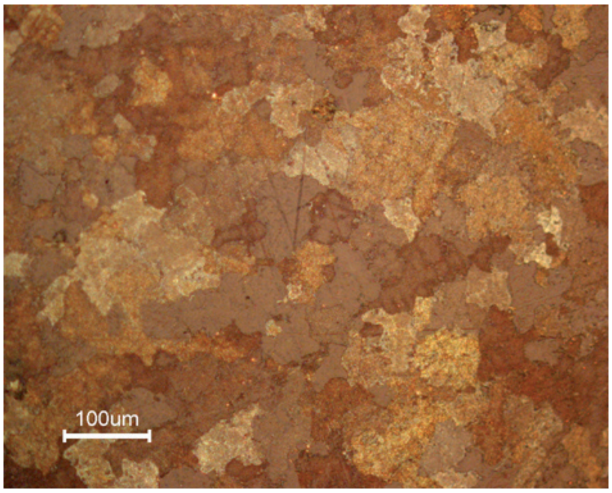

Figure 6 - Grain of Alloy 15 after mold casting

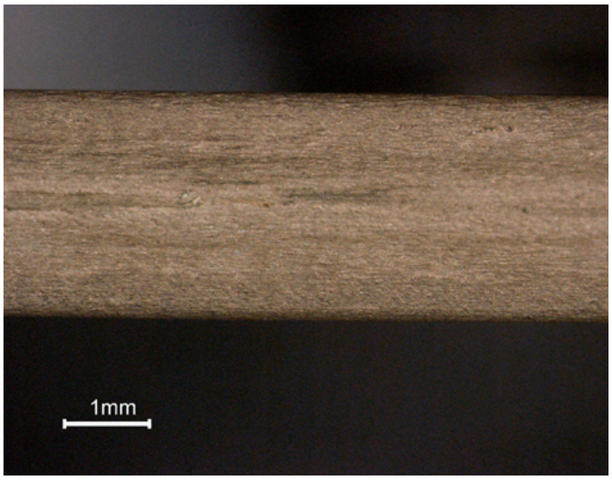

Figure 7 - Side of Alloy 15 after a 75% deformation

Once analyzed the effect of nickel and tin we checked what could happen with the addition of nickel and gallium. Table 3 shows the tested compositions.

Table 3 – Ni-Ga compositions

Alloy	Au	Ag	Zn	Cu	Ni	Ga	Ir
19-Ag10Zn10Ga10Ir	917	10	10	52,85	-	10	0,15
20-Ag5Zn5Ni9Ga10Ir	917	5	5	53,75	9,1	10	0,15
21-Ag5Zn5Ni8Ga10Ir	917	5	5	54,9	8	10	0,1
22-Ag5Zn5Ni8Ga6Ir	917	5	5	58,9	8	6	0,1
23-Ag5Zn5Ni6Ga12Ir	917	5	5	54,9	6	12	0,1
24-Ag5Zn5Ni9Ga12Ir	917	5	5	51,8	9,1	12	0,1
25-Ag5Zn5Ni12Ga12Ir	917	5	5	48,9	12	12	0,1

In this case the compositions were selected as function of the results obtained with the addition of nickel and tin; then, we checked the threshold of nickel quantity (found out around 9.1‰) and the suitable gallium quantity (tin one was about 11‰). Besides, experience acquired with other papers[6] made us add a different grain refiner with gallium (to be precise, iridium).
Alloy 19 (Ag10Zn10Ga10Ir) did not contain nickel, to verify if a hardening could be obtained the same. Alloy 20 (Ag5Zn5Ni9Ga10Ir) had the composition of the sample with tin which gave us the maximum hardness, that is Alloy 15 (Ag20Zn3-Ni9Sn11Re). In left Alloys we changed the content of nickel and gallium, to understand by what limit we would not obtain an hardness increase and, in case of Alloy 25 (Ag5Zn5Ni12Ga12Ir), to define what hardness value could be reached. The quantity of silver and zinc was lowered to 5‰, to obtain a more intense yellow color, as nickel, gallium and tin tend to whiten a lot.

Figure 8 shows the trend of hardness for these samples, all hardened at 300°C for 180 minutes (seen the previous tests results we did not carry out the hardenings at 250 and 400°C), after an annealing at 700°C for 18 minutes.

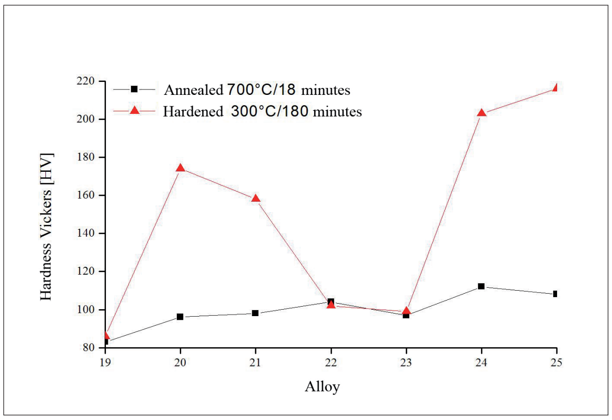

Figure 8 - Hardness values measured after annealing and after hardening at 300°C for 180 minutes

You can also notice that with the addition of nickel and gallium a considerable hardening could be obtained by heat treatment. Gallium without nickel was not able to confer any hardness increase to the material (as tin). Even in the case of nickel-gallium there was a minimum threshold of the two elements under which no hardening could take place. Nickel threshold is about 8‰, while gallium should be embedded between 8 and 10‰ — this was not checked, but Alloy 22 hardness did not increase while Alloy 21 gave 160HV only passing from 6‰ to 10‰ of gallium. It was also evident that as nickel and gallium contents increased, the hardness notably increased (it seemed in a linear way, but we did not get enough data to state it), reaching about 220HV.
Figures 9 and 10 show Alloy 21 (Ag5Zn5Ni8-Ga10Ir) microstructure after mold casting and the rolling side after a 75% reduction.

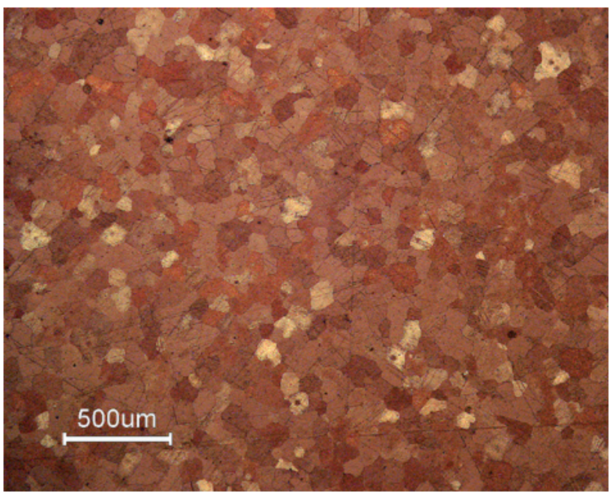

Figure 9 - Grain of Alloy 21 after mold casting

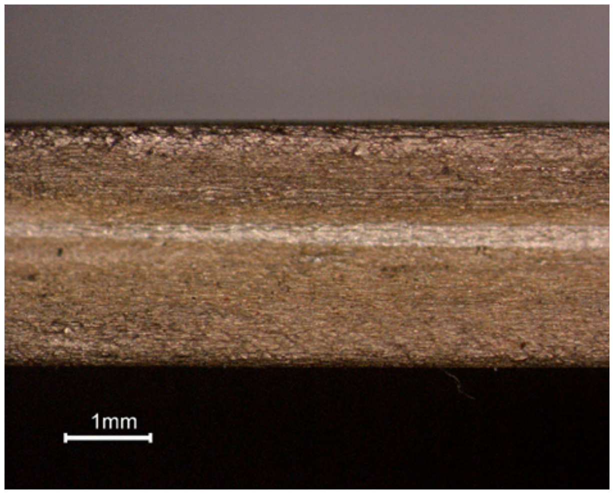

Figure 10 - Side of Alloy 21 after a 75% deformation

Once verified that nickel-tin or nickel-gallium after proper heat treatment could allow reaching hardness values above 160HV, we checked the results obtained by the addition of these three elements together. Then we prepared the Alloys shown on table 4.

Table 4 - Ni-Ga-Sn [‰] compositions

Alloy	Au	Ag	Zn	Cu	Ni	Ga	Sn	Re
26-Ag5Zn5Ni9Ga10Sn11Re	917	5	5	42	9,1	10	11	0,9
27-Ag5Zn5Ni9Ga10Sn7Re	917	5	5	46	9,1	10	7	0,9
28-Ag5Zn5Ni9Ga10Sn3Re	917	5	5	50	9,1	10	3	0,9
29-Ag5Zn5Ni7Ga10Sn2,3Re	917	5	5	53	7	10	2,3	0,7

Alloy 26 had the same quantity of nickel, gallium and tin which supplied the maximum measured hardness values. We lowered the tin quantity in Alloys 27 and 28, keeping constant the content of nickel and gallium. We reduced the quantity of nickel and tin in Alloy 29, keeping constant the gallium content. We used rhenium as grain refiner.
Figure 11 shows the trend of hardness for these samples, all hardened at 300°C for 180 minutes after annealing at 700°C for 18 minutes.

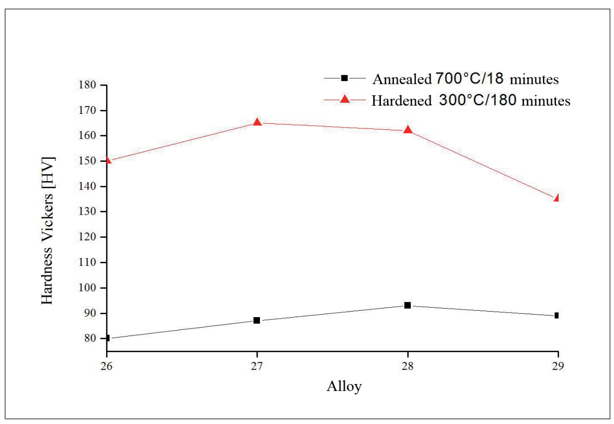

Figure 11 – Hardness values after annealing and after hardening at 300°C for 180 minutes

From this graph you can see that as nickel quantity decreased to 7‰, the hardness slightly decreased, confirming that the inferior threshold of nickel content to get an acceptable hardness was probably 8‰. The contemporaneous addition of gallium and tin did not alloy reaching the values of hardness measured with the only single elements (obviously with nickel). Tin seemed to negatively interfere with gallium as far as hardness is concerned; in fact, Alloy 26 displayed 24HV less than Alloy 20, which had the same content of nickel and gallium. We found interesting the fact that Alloy 28, with a content of gallium and tin equal to 12.3‰ (that is Ga+Sn=12.3‰) displayed 90HV of hardness less than Alloy 25, which content of gallium was around 12‰.

3. Discussion about the results

With the traditional quaternary alloys (Au, Ag, Zn and Cu) it is not possible to obtain a higher hardness, as the quantity of master alloy alloyed with gold is not sufficient to guarantee a hardening according to the mechanisms valid for the golden alloys. This means that:

- there is not a sufficient quantity of copper to form a super-structure (as it happens in 18K, solid solution of ordered substitution), but there are only limited ordered zones in the alloy, so the maximum reachable hardness is around 90HV.
- there is not a contemporaneous presence of silver (and copper) sufficient to produce a hardenable microstructure by precipitation (see copper-silver phase diagram).

As far as the alloys containing cobalt are concerned, we saw that only high cobalt contents (around 20‰) allow reaching high hardness values, as hardening occurs for precipitation. Small Cobalt additions, even when associated with other impurities, do not increase alloy hardness.

The addition of nickel-tin gives the alloy a notable hardness. But we saw that a threshold quantity exists and under this limit hardening does not take place. This inferior limit is 9‰ for nickel and 11‰ for tin (but this was not deeply investigated). In any case, among the compositions we tested, the one displaying the higher hardness values contained 9.1‰ of nickel and 11‰ of tin (it allowed reaching about 154HV). From literature, more specifically from the analysis of the Ni-Sn phase diagram, it came out that it is possible to obtain a solid solution of ordered substitution (actually, the four empiric rules of Hume-Rothery are satisfied)[5]. Transforming in atomic ratio and considering the nickel-tin ratio, you can trace back to the chemical formula Ni3Sn2, which can form a super-lattice4 under 600°C (see figures 12 and 13). Then we supposed that the hardness increase is due to a precipitation of the Ni3Sn2 super-structure (coherent or incoherent, this has to be checked), Literature says that there is a Cu2NiSn super-lattice as well[7].

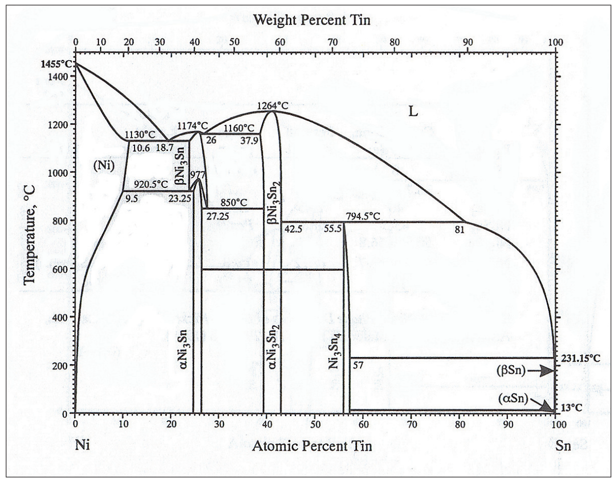

Figure 12 – Ni-Sn phase diagram

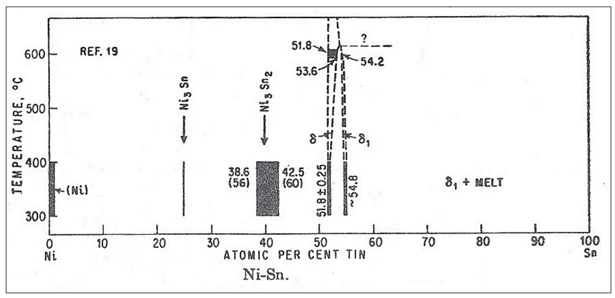

Figure 13 – Part of Ni-Sn phase diagram take into consideration[4]

As far as gallium is concerned, We found in literature that there is a Ni3Ga with Cu3Au super-lattice. This ordered phase (formed due to a restricted composition) produces a noticeable difference in reticular parameters of the two coexisting cubic phases[4] [7]. Therefore, we hypothesize that the mechanism allowing hardening is the same seen with tin. In particular, we observed that the minimum nickel quantity to add is 8‰ and gallium one is 10‰ (hardness reached: 158HV), which is equal to an atomic ration of 1, that is the Ni-Ga formula (in atomic percentage, this corresponds to 48.7% Ni and 52.3 Ga). We could also see that, adding 12‰ nickel and 12‰ gallium you can reach a hardness of 218HV, which is equal to the formula Ni3Ga2.

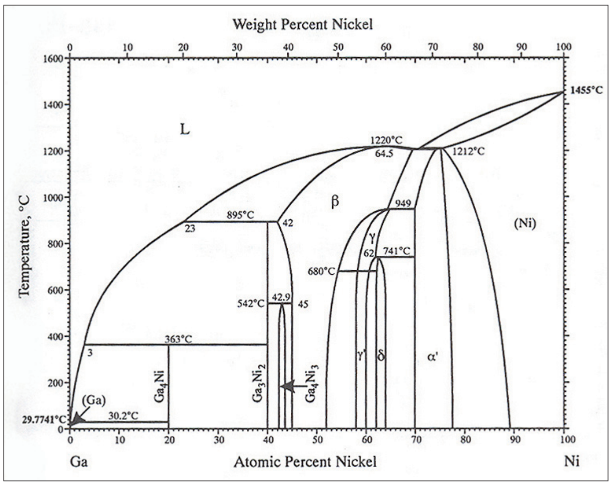

Figure 14 – Ni-Ga phase diagram

These hypothesis would justify the fact that adding gallium and tin together hardness does not increase. On the contrary, it decreases, as nickel present in alloy is not enough for the compositions allowing the formation of ordered phases (these composition intervals are very close).

Seen the obtained results, we also checked if indium and germanium could supply the same hardening capability given by gallium and tin. We checked with indium and germanium because they are the closest elements, in the periodic table, to gallium and tin and then they are supposed to have the closest characteristics as well – even if indium has a wider atomic radius than the other elements and so it does not satisfy the dimensional factor given by the Hume-Rothery rules.
We tested four new Alloys (see table 5).

Table 4 – Composition with Ge and In [‰]

Alloy	Au	Ag	Zn	Cu	Ni	In	Ge
30-Ag5Zn5Ni9Ge5	917	5	5	59	9	-	5
31-Ag5Zn5Ni9Ge15	917	5	5	49	9	-	15
32-Ag5Zn5Ni9In10	917	5	5	54	9	10	-
33-Ag5Zn5Ni9In20	917	5	5	44	9	20	-

In these samples we kept constant the quantity of silver, zinc and nickel (9‰). In Alloy 30 we added 5‰ of germanium and in Alloy 31 we added 15‰. We added 10‰ of indium in Alloy 32 and 20 ‰ in Alloy 33. Figure 15 shows the hardness trend for these alloys, all hardened at 300°C for 180 minutes after an annealing at 700°C for 18 minutes.

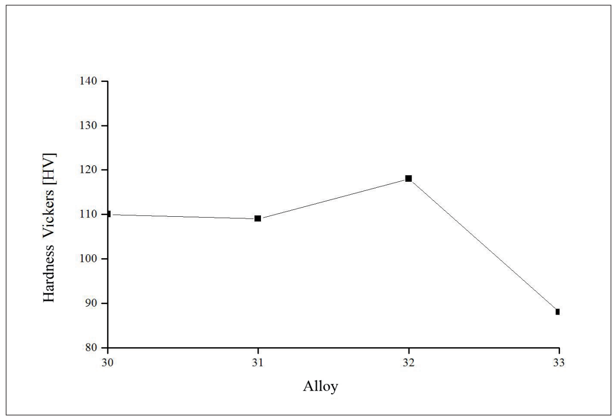

Figure 15 – Hardness values after annealing at 300°C for 180 minutes

As you can see, germanium did not give an important hardness increase. Probably, another systematic analysis is necessary, as that carried out in case of gallium and tin. In any case, we observed that the sheets were much oxidized after the different heat treatments, while with gallium they were completely deoxidized.

As far as indium is concerned, we saw a hardness peak adding 10‰, while doubling its quantity we noticed an abrupt change of hardness. Probably, the reached hardness depended on what phase formed and in case of indium it is fundamental to obtain Ni3In, while with 20‰ of indium you can probably obtain the Ni-In phase (this is just an hypothesis). Figure 16 shows the Ni-In phase diagram.

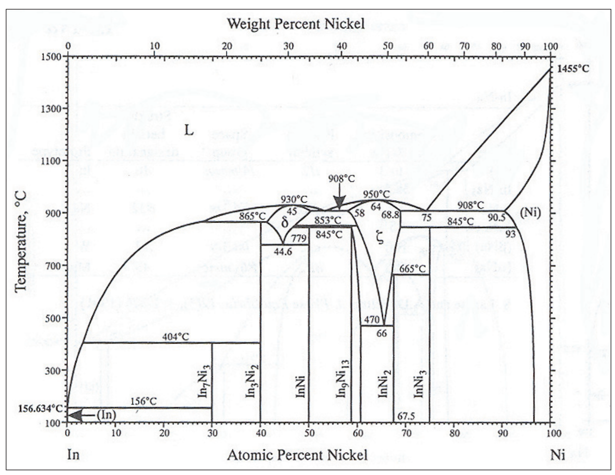

Figure 16 – Ni-In phase diagram[4]

Anyways, more investigations are necessary to verify what above reported. All these hypothesis were formulated only on the basis of theoretical considerations. In addition to germanium and indium, also antimony (Sb) is supposed to allow hardening[8].

4. Conclusions

The results we obtained made us state that the hardening of 22K gold alloys is possible even without using cobalt (after proper heat treatment) with the use of a master alloy to add to pure gold. We chemically determined that, associating nickel with gallium or tin (in determined ratios) you can easily obtain hardness values of about 160-170HV (also to 220HV, but to the detriment of the color), comparable with the values of hardness after casting of 18K gold alloys. We prepared some trees with alloys containing Ni-Sn and Ni-Ga, to check their behavior in investment casting. The best results were obtained with the Ni-Ga alloy. The Ni-Sn alloy displayed a surface with dendritic structure and an evident shrinkage after casting, as you can see in figure 18.

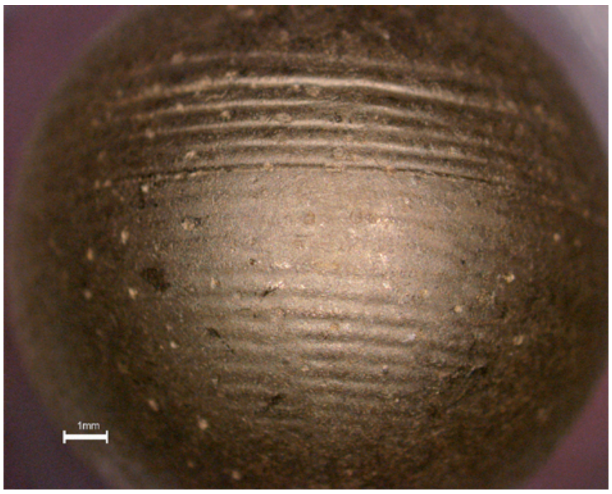

Figure 17 – Sphere obtained with Alloy 20 (Ag5Zn5Ni9-Ga10Ir)

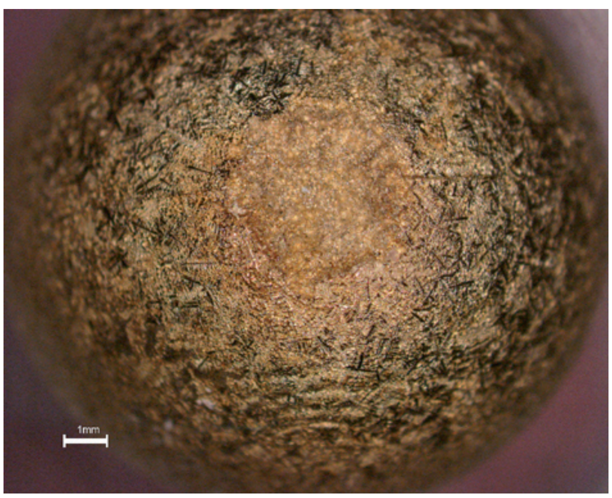

Figure 18 – Sphere obtained with Alloy 15 (Ag20Zn3-Ni9Sn11Re)

We hypothesize that this problem could depend on the fact that tin produces phases with low melting range, with a consequent widening of the melting range. We also used silicon (in different concentrations) to check its effects[6], whose results will be reported in another paper.

Gallium, besides allowing reaching higher hardness values than tin, guarantees a higher surface quality in items obtained by investment casting.

In conclusion, the hardenable master alloy for 22K yellow gold supplying the best results both in investment casting and in mechanical working is an alloy with at least 8‰ of nickel and 10‰ of gallium (in the master alloy).
The hardness values reached are higher than 160HV. The possibility of reaching these hardness values involves notable advantages in the production cycle, such as a higher ease in working (the items are more resistant at indentations) and the possibility of using mechanical finishing treatments (such as sieving and/or hand finishing by brushes). Consequently, it is possible to obtain products with a very high brightness.

These hardness values allow obtaining articles with very thin thickness (e.g. super-light) and articles such as filigrees, currently difficult to produce. Also the possibility of realizing new articles with shapes and geometries which were not feasible before has to be taken into consideration.

In this work we reported the measured hardness values and some theoretical hypotheses about the hardening mechanisms. We are still investigating their applicability to other finenesses.
Certainly this principle will be applied to obtain a hardenable white alloy for 22K.

5. Bibliography

1. ProGold patent n° VI2004A101, April, the 30th 2004, “Master alloy for the production of 21-22ct precious pieces, which added to gold can grant a hardening yellow alloy, with low defect concentration”
2. C.W. Corti, “Oro a 24 carati ad alta resistenza: la metallurgia della microalligazione” Gold Technology, winter 2001, pages 23-32
3. Daniele Maggian, “Comparison of different methods used to establish recrystallization condition of gold alloys”, Acts of 17th Santa Fe Symposium, 2003, pages 197-226
4. Max Hansen & Kurt Anderko, Constitution of Binary Alloys, McGraw-Hill 1985
5. G.M. Paolucci, Metallurgia vol.1, Libreria Progetto, Padova 2000
6. Iader Milani, Daniele Maggian, Silvano Bortolamei, Acts of Saint Petersburg Symposium 2004
7. Charles Barrett and T.B. Massalski, Structure of Metals 3rd revised edition, Pergamon Press, 1980
8. Jörg Fischer-Bühner, FEM, private communications, 2004
9. Hubert Schuster, Jewellery Technology Institute, private communications, 2004