

Abstract

Knowing gold alloys characteristics enables to get precious information for selecting the most suitable alloy composition for each particular production process.

Obviously, in the case of gold alloys, color plays a fundamental role in the selection of the composition to be used, but in all cases minor additions of some specific elements can contribute to improve some characteristics that are important in the production process.

On the basis of these considerations, we decided to determine the chemical and physical properties of several 9, 10, 14 and 18 ct gold alloys.

The aim of this work was to correlate the characteristics of each alloy with the chemical composition, to be able to select the gold alloy representing the optimum solution for the different practical uses. Considering the high cost of the alloys, we have refined some methods for evaluating the properties of precious alloys (or, better, we improved evaluation methods already used in different industry sectors), to obtain the data required to achieve this goal.

Introduzione

The study of materials properties is very important in all industry sectors, to select the most suitable material for each production process and practical use. In our case, we need to study the properties of gold (and silver) alloys for jewelry production. Therefore we decided to develop evaluation methods enabling to get information on the behavior of gold and/or silver base alloys, to be able to use the correct composition for each purpose. Obviously, we focused our efforts into determining physical, chemical and mechanical properties of the materials under study, but we are also looking forward to develop technological tests to evaluate alloy properties for specific uses (e.g. corrosion resistance during core dissolution processes).

Summing up, we aim to characterize 9, 10, 14 and 18 ct gold alloys, and subsequently to analyze the obtained data, to select the most appropriate composition for obtaining the required characteristics.

To be more specific, we emphasize that in the usual practice gold alloys for jewelry are subdivided on the basis of caratage and color, but up to now there is not a classification based on mechanical characteristics. The ambitious aim of this work is to create a handbook of the characteristics of precious alloys, enabling to select the most suitable one for each production process.

Obviously this handbook should be systematically updated with new data for new alloys, to have more information available for an ever increasing number of alloy compositions. It should be remembered that very often the final color (and not the technical characteristics) is the only selection criterion, but the availability of data enables to say if a given composition can give good results or if it requires special techniques – e. g. lower deformation – to produce the final object. We believe that numerical, objective and comparable data will enable to compare different alloys, to find the best compromise between the specified requirements and the production process.

Our work has been subdivided into three parts. The first part includes the study and development of the tests for the determination of the required characteristics. The second part includes the collection and analysis of data on the chemical and physical properties of each alloy. The third part includes the definition of the parameters more connected with the specific production processes, to readily find the most suitable alloy, or even to be able to make a classification of alloys for each type of production process. Only part 1 and a portion of part 2 will be treated in this paper. Part 1 will be exhaustively illustrated, while part 2 will be limited to 18 ct alloys.

All the compositions taken into consideration correspond to alloys produced by our company, but obviously they were not named with the corresponding commercial code, but a conventional code was used. We emphasize that our testing methods are based on European or ASTM standards developed for different industry sectors (mainly steel industry).

Presently, if we do not consider color and caratage, the alloys are commonly classified on the basis of two main production processes:

1. Alloys for investment casting

2. Alloys for wrought products.

This classification has been followed also in our paper for the sake of clarity.

The main difference between the above alloy classes usually (but not always) is that alloys of the first class contain specific deoxidizing elements (deoxidizers), while the alloys of the second class do not contain deoxidizers. All of them and can contain grain refiners.

The alloys we studied are quaternary alloys with minor additions of different elements that give specific properties. The various compositions have also been subdivided into two families.

1. The first family includes "colored" gold alloys. They have a quaternary Au-Ag-Cu-Zn basis, with minor additions of various elements. We called these alloys "colored" because the obtainable colors range from deep red to green through various hues of yellow.

2. The second family includes "white" gold alloys. They have a quaternary Au-Ni-Cu-Zn basis, with minor additions of various elements. These alloys are called "white" because they show various hues of white (or we could say of "grey").

The results will be presented according to this classification.

Characterization method

The characterization method we developed is described below.

Each alloy was pre-melted (800 g for 18 ct alloys, 700 g for 14 ct alloys, 600 g for 9 ct and 10 ct alloys). We used an open, induction heated, furnace with a graphite crucible and subsequent casting into ingots. An open furnace was used to allow mechanical mixing for better homogeneity.

The pouring temperature depended on caratage

and color and the alloys were subdivided into groups on the basis of composition. The metal was protected by blowing inert gas in the crucible during melting and pouring. Then the ingots were rolled and cut into pieces for the second melting operation in a closed casting machine with controlled atmosphere. After pre-melting, alloy samples were submitted to DTA analysis, and a pouring temperature 100° C higher than the measured liquidus point was used in the closed casting machine.

For each composition, a maximum of five casting operations were carried out in the closed casting machine, using pre-melted material. Ingots and investment cast specimens were obtained for the subsequent characterization. Namely:

1. $20 \ge 8$ mm rectangular cross section ingots for the work-hardening tests and for producing the specimens for density measurement, color tests (and nickel release tests). These ingots were cast for all compositions.

2. 70 x 5 mm rectangular cross section ingots for producing specimens for the deep drawing tests. These ingots were cast for wrought alloys only.

3. 6×6 mm square cross section ingots for wire drawing for the tensile tests on wrought material. These ingots were cast only for wrought alloys.

4. A ask with 16 specimens for the hardness tests and the determination of the average grain size $(24 \times 12 \text{ mm}, 4 \text{ mm} \text{ thick plates})$ These specimens were cast for all compositions.

5. A ask with 30 test pieces for tensile tests on investment cast material. These specimens were cast only with the alloys for investment casting.

The closed casting machine was formed of two communicating chambers. The mold or the ask was introduced in the lower chamber and the crucible for melting was contained in the upper chamber. Pouring takes place through a hole in the crucible bottom, by lifting a rod plugging the hole.

The molds were preheated to 320°C in an oven. The dimensions of the molds are suitable for introducing them in the casting machine with controlled atmosphere. The preheated mold was put in the machine after filling the crucible with the metal charge, but before closing the machine and starting the casting cycle (an automatic program was used). This procedure was preferred, to cast ingots of all alloys in the same conditions and to avoid errors that could be caused by manual operation.

After casting, the mold chamber was quickly opened and the ingot was immediately water quenched.

The ask with the plates was preheated at 600°C

and the ask with the specimens for tensile tests was preheated at 700°C, to avoid incomplete filling. In this case too the asks were put in the casting machine before closing and starting the casting cycle. After casting, the asks were water cooled after 6 minutes for alloys containing grain refiners or after 20 minutes for alloys containing only deoxidizers.

The 20 mm wide and 8 mm thick ingot was rolled with a set of rolling passes, to determine the work hardening curve of the alloy. Hardness was measured on the as cast metal (8 mm thickness), after 40% rolling reduction (5 mm thickness), after 60% reduction (3 mm thickness), after 80% reduction (1,5 mm thickness) and after 90% reduction (0,8 mm thickness). Ten 16 x 8 mm specimens were cut from the 1,5 mm thick sheet for density measurement (5 specimens) color tests (2 specimens) and annealing tests (3 specimens). Hardness of the annealed specimens was measured.

The work hardening curve was determined only for the wrought alloys. The alloys for investment casting were rolled directly from 8 mm to 1,5 mm thickness, then the various specimens were cut. The nickel containing alloys were rolled to 2 mm thick sheet. The sheet was cut into two parts and a part was annealed. Then the thickness was reduced to 0,5 mm and three 12 mm diameter disks were cut (with a central 1 mm diameter hole) for the nickel release test, according to the Standard UNI EN 1811.

The 70 mm wide and 5 mm thick ingot was rolled to 2 mm thickness and then annealed. After further rolling to 0,4 mm thick sheet, five 70 x 70 mm wide specimens were cut. These specimens were annealed in suitable conditions (see Table 1) and were used for the deep drawing tests.

The 6 x 6 mm square section ingot was rolled to 1 x 1 mm square section wire for the tensile tests, with the following rolling schedule. Rolling from 6 x 6 to 4 x 4 mm square section (55% reduction) – annealing – rolling from 4 x 4 to 2 x 2 mm square section (75% reduction) – annealing – rolling from 2 x 2 mm to 1 x 1 square section - final annealing. The 1 x 1 mm wire was used for the tensile tests. Tensile tests on wire are carried out only in the case of wrought alloys.

The annealing parameters depended only on alloy composition, according to Table 1.

Caratage	Temperature [°C]	Time [min]	Cooling	
9, 10, 14ct white	725	18	Fast in oil	
18 ct 700		18	Fast in oil	

9, 10, 14ct colored	675	18	Fast in water
18ct colored	650	18	Fast in water

Table 1 - Parameters for annealing heat treatments

In all cases annealing was carried out in a static laboratory oven, under reducing atmosphere.

The ask with the $24 \ge 12 \ge 4$ mm plates was produced for determining the hardness of the alloys as cast or after different heat treatments, i.e.:

- 1 plate as cast,

- 1 plate after solution heat treatment,

- 9 plates after age hardening at different temperatures for different time.

The parameters for the solution heat treatment (temperature, time) depended on composition, according to Table 2.

Caratage	Temperature [°C]	Time [min]	Cooling
9, 10, 14ct white	750	30	Fast in oil
18ct white	725	30	Fast in oil
9, 10, 14ct colored	700	30	Fast in water
18ct colored	675	30	Fast in water

Table 2 - Parameters for the solution heat treatment

The age hardening heat treatment was carried out on all alloys (irrespective of composition) at 250, 300, 350°C. Holding time in the oven was 60, 120 and 180 minutes for each temperature. Therefore we had 9 hardened specimens. All the specimens were solution heat treated before hardening, according to Table 2, and water quenched after hardening.

The hardening characteristics were verified on investment cast, undeformed specimens, after suitable heat treatment. This procedure is easier and faster and even if it does not enable to find the highest attainable hardness, it enables to identify the hardenable alloys precisely. Anyway, the data for precipitation hardened specimens are comparable, and it is possible to obtain a classification of the alloys in order of hardenability.

The ask with the investment cast tensile test pieces was produced only for the alloys for investment casting. The test pieces had a 2 mm diameter and a 12 mm utilizable length (L0), Figure 1.



Figure 1 - Test piece for tensile tests

After the preparation of the various test pieces, data were collected by means of the tests we will describe below. We will not dwell on details, because each test corresponds to an European or ASTM Standard.

DTA test

The Different Thermal Analysis (DTA) test enables to find the solidus and liquidus temperatures (i.e. the melting range) of alloys. A 25 mg pressed specimen was used. The DTA test was carried out on the pre-melted metal to find the pouring temperature in the closed machine and again for confirmation on a sample from the alloy cast in the closed machine (the alloys are more homogeneous after the second melting operation).

Density measurement

The density of the alloys was measured thanks to the Archimede's principle that says that a body dipped in a liquid feels a positive buoyancy equal to the weight of the liquid displaced by the specimen's volume.

The following formula was used to calculate density:

d = w(a) * d(f1) [w(a) - w(f1)]

where:

d = density of the solid specimen d(f l) = density of the liquid w(a) = weight of the solid specimen in air w(f l) = weight of the solid specimen in the liquid

The work hardened 16 x 8 mm 1,5 mm thick plates (5 specimens) were used for density measurements.

Deep drawing test

The drawability was evaluated by measuring the displacement of the punch when the specimen (a $70 \ge 70 \mod 0.4 \mod$ thick sheet) starts breaking. This information is very important for the pro-

duction of "stampato".

The value of drawability corresponds to the height of the cup (in mm) produced by the punch in the sheet. The punch is formed of a 20 mm diameter steel sphere and is gradually pushed against the sheet specimen until the operator detects the initiation of a crack. The sheet is fastened with a clamping device to avoid sliding during the test. This is practically the Erichsen method, see ASTM Standard E 643-84.

Tensile test

The tensile test enables to measure the ultimate tensile stress (UTS), the yield strength (YS) and the percent elongation to rupture (E%). The first two parameters give an evaluation of the mechanical strength, while the third one refers to the ductility of the material.

UTS is defined as the ratio between the maximum applied load and the cross section area of the tensile specimen before loading. It is a characteristic property of the material. More specifically, UTS is the maximum uniaxial stress the material can tolerate before breaking. The yield strength is the stress corresponding to the beginning of plastic deformation, i.e. to the transition from an elastic reversible deformation to an irreversible plastic deformation. In this work the 0,1% deformation yield strength (YS0,1) was considered.

The deformation to rupture, commonly named percent elongation, is denoted with E% and is measured as the length of the ruptured tensile specimen, expressed as the percentage increase of the initial usable length of the specimen.

The tensile test was carried out on two different types of specimens, depending on the alloy type, i.e. an alloy for investment casting or a wrought alloy.

In the case of alloys for investment casting the tensile specimens were directly obtained from the

ask cast for this specific use. Therefore these tensile specimens must be accurately inspected to reduce the number of defective tests to a minimum: i.e. the specimens must be free from visible defects and perfectly centered. If, in the tensile test, the rupture occurs out of the usable length (L0 Figure 1) the result is discarded, because it is believed that stress concentration near the change of cross section could alter the result of the test. To have a usable result of the test, the results of at least 15 valid tensile specimens were considered: the final result is the average of these tests. Also the clamping device was carefully designed, to reduce clearance and positioning error of the test pieces to a minimum.

In the case of wrought alloys, a square cross sec-

tion 1 x 1 mm wire was used, with a 200 mm usable length. The samples were annealed after rolling and carefully inspected, to avoid visible surface defects. A pneumatic clamping device with partial wire winding was used. Rupture of the wire must take place between the clamps, to have a valid result. In this case too a minimum of 15 valid tests was averaged. ASTM E8-00 was the reference standard.

In the case of alloys suitable both for investment casting and for plastic deformation, the tensile tests were carried out both with as cast and with wire specimens.

Hardness test

The hardness of the materials was measured in various conditions: as cast, work hardened, annealed, solution heat treated, precipitation hardened. The Vickers method was followed, with a 500 g load for 15 s. See ASTM Standards E 92-82 and E 384-99. More precisely, the hardness was measured on specimens treated as follows:

1. Work hardened: as cast; after 40%, 60%, 80% and 90% rolling reduction. These measurements were carried out only on the alloys suitable for plastic deformation.

2. Annealed: 80% rolling reduction, followed by annealing in accord with the parameters of Table 1.

3. Heat treated: the plate specimens were: as cast, solution heat treated, precipitation hardened in 9 different conditions (temperature and time).

Measurement of grain size

The average grain size was measured according to the Jeffries method, i.e. by counting the number of grains present in a predetermined area. The as cast specimens were carefully polished and submitted to a metallographic etching with a cyanide solution to make grains visible. See the ASTM Standard E 112-96.

The grain size was measured only on as cast specimens, not on annealed specimens, both for investment cast and wrought alloys.

Color evaluation

The CIELab color coordinates were determined from the coefficients of re ection measured on test specimens specifically prepared for this purpose (work hardened and lapped 16 x 8 mm plates). The re ection spectra of the specimens are computer processed (see ASTM Standard E 308-99) to obtain the CIELab color coordinates (L*, a* and b*). A single point in the three-dimensional color space is identified for each alloy composition.

Measurement of the nickel release rate

This test is designed to simulate the nickel release rate from articles coming in direct and prolonged contact with the human skin. The UNI EN 1811 Standard was carefully followed. The geometry of the specimens of the different alloys conformed with the directions of the above Standard. At the end of the test period, the concentration of dissolved nickel in the solution was determined through plasma spectroscopy (ICP-OES). The nickel release rate was then given as mg/cm2/ week and the corrected value was taken into account.

The nickel release rate was measured only on nickel containing alloys, i.e. on white golds.

Data processing

After establishing the practice for each characterization test, data were gathered for all alloys we are producing. We emphasize that there are "universal" alloys that are suited both for investment casting and plastic deformation. For these alloys all the above described tests were carried out. The results obtained for the 18 ct colored gold alloys are described in the following paragraphs.

18 ct colored gold alloys

Thirty-four alloy compositions were investigated. The compositions of these alloys are listed in Table 3, where they are ordered according to the silver concentration (and, secondly, according to the zinc concentration). In Table 3 GR1 denotes a type of grain refiner and GR2 denotes another type of grain refiner.

Spec- imen	Au	Ag	Zn	Cu	GR1	GR2	Deoxi- dizers
Alloy 1	750	3,75	3,75	Bal- ance	Х		
Alloy 2	750	8,75	8,75	Bal- ance	Х		
Alloy 3	750	10	7,5	Bal- ance		Х	
Alloy 4	750	25	5	Bal- ance	Х		
Alloy 5	750	25	7,5	Bal- ance		Х	
Alloy 6	750	42,5	11,25	Bal- ance	Х		
Alloy 7	750	45	2,5	Bal- ance	Х		

Alloy 8	750	45	2,5	Bal- ance		Х	
Alloy 9	750	45	12,5	Bal- ance		Х	
Alloy 10	750	72,5	7,5	Bal- ance			Х
Alloy 11	750	75	62,5	Bal- ance		Х	
Alloy 12	750	75	62,5	Bal- ance			Х
Alloy 13	750	77,5	26,25	Bal- ance		Х	
Alloy 14	750	80	5	Bal- ance		Х	
Alloy 15	750	110,5	4,75	Bal- ance		Х	
Alloy 16	750	112,5	25	Bal- ance		Х	
Alloy 17	750	115	8,75	Bal- ance			Х
Alloy 18	750	117,5	5	Bal- ance	X		
Alloy 19	750	117,5	5	Bal- ance		X	
Alloy 20	750	117,5	5	Bal- ance			X
Alloy 21	7504	118,75	28,75	Bal- ance		X	
Alloy 22	750	120,5	20,5	Bal- ance			Х
Alloy 23	750	121,5	9	Bal- ance		Х	
Alloy 24	750	123	8,75	Bal- ance			Х
Alloy 25	750	125	26	Bal- ance			Х
Alloy 26	750	137,5	17,5	Bal- ance		Х	
Alloy 27	750	141,25	8,75	Bal- ance		Х	
Alloy 28	750	141,25	8,75	Bal- ance			Х
Alloy 29	750	143	8	Bal- ance			Х
Alloy 30	750	150	11,25	Bal- ance	Х		
Alloy 31	750	155	3,75	Bal- ance		Х	
Alloy 32	750	160	8,75	Bal- ance		Х	
Alloy 33	750	160	8,75	Bal- ance			Х
Alloy 34	750	190	3,75	Bal- ance	X		

Table 3 - Composition of the 18 ct investigated coloredgold alloys (weight ‰)

Initially, the variation of liquidus and solidus temperatures was investigated. The results are plotted in Figure 2 for all studied alloys.

The triangles correspond to liquidus tempera-

tures, the squares correspond to solidus temperatures. The upper continuous curve is the best fit of the liquidus temperatures, with the exclusion of the alloys containing more than 12,5 wt‰ zinc, i.e. alloys 11, 12, 13, 16, 21, 22, 25 and 26 (only 24 alloys were considered for the best fit curve). As can be expected, an increasing zinc concentration lowers the liquidus temperature, but this aspect was not considered for the moment. It is interesting to see that with an increasing silver concentration the liquidus temperature is initially lowered and then increased.

The lower continuous curve of Figure 2 is the best fit of the solidus temperatures, with the exclusion of alloys 11, 12, 13, 16, 21, 22, 25 and 26, as above said. In this case too with an increasing silver concentration the solidus temperature is initially lowered and then increased.



Figure 2 - Graph of liquidus and solidus temperatures (°C) against silver concentration (wt‰)

It should be observed that the difference between the liquidus and solidus best fit curves (i.e. the melting range) increases with increasing silver concentration. This increase can be more clearly observed in Figure 3, where the melting range of the above considered alloys (zinc concentration lower than 12,5‰) is plotted vs. the silver concentration.



Figure 3 - Graph of the melting range (°C) against silver concentration (wt‰)

In Figure 3 also the deoxidizers containing alloys have been excluded, because it is well known that elements such as silicon tend to widen the melting range. Although we excluded several alloys, we can see that an increase of silver concentration tends to widen the melting range.



Figure 4 - Graph of the density (g/cm3) against silver concentration (wt‰)

Figure 4 shows that density increases with silver concentration. In this case too the best fit curve was calculated with the exclusion of alloys containing more than 12,5% zinc. Zinc in unces the density value, but silver is the element affecting density more noticeably.



Figure 5 - Graph of L* against silver concentration (wt%)

The results for L* color coordinate are plotted in Figure 5 against silver concentration (wt‰). In this case too the best fit curve (continuous curve) was calculated with the exclusion of alloys containing more than 12,5‰ zinc. It can be seen that L* increases with increasing silver concentration. Moreover (even if the data were scarce) it appears that also an increasing concentration of zinc can increase L*. It appears that small additions of grain refiners or deoxidizers scarcely affect the value of L*.

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When we consider the value of a^{*}, Figure 6, we see that with an increased silver concentration the color is shifted from red to green (it should be remembered that a^{*} represent the "color dimension" going from red to green).

In this case too the best fit curve (continuous curve) was calculated with the exclusion of the alloys containing more than 12,5% zinc. It could be interesting to consider the variation of a* as a function of copper concentration instead of silver (this is approximately comparable to considering the sum silver + zinc, because the amount of other additions is small). But zinc seems to be more effective than silver for shifting the color from red to green. In our opinion the zinc seems to show an effect two times stronger than silver, even if it should be better to consider different composition ranges. To verify this effect a larger number of compositions with various zinc concentrations and constant silver concentration should be studied.

In Figure 7, a^* is plotted against the silver concentration added to two times the zinc concentration. Figure 7 seems to confirm the hypothesis that the effect of zinc is about two times stronger than the effect of silver. In this case the best fit curve was calculated taking into account all the studied alloys, no one excluded.



Figure 6 - Graph of a* against silver concentration (wt%)



Figure 7 – Graph of a* against silver concentration added to two times the zinc concentration (wt%)

The value of b* is shifted towards the yellow when silver concentration is increased (b* represents the "color dimension" going from yellow to blue). As usual, the best fit curve does not take into account the zinc rich alloys.



Figure 8 – Graph of b* against silver concentration (wt%)

The effect of zinc on b^* seems to be weaker than in the case of a^* , but it should be confirmed with the study of some suitable alloy compositions. It seems that the effect of zinc could be similar to the effect of silver when the value of b^* is considered. Therefore we can plot b^* against copper concentration (i.e. concentration of silver added to zinc concentration).



Figure 9 – Graph of b* against copper concentration (wt%c)

In this case all alloys, no one excluded, were used for drawing the best fit curve. This diagram shows that the effect of zinc concentration on b^* is lower than on a^* .



Figure 10 – Graph of hardness against silver concentration (wt‰)

Figure 10 shows the effect of silver concentration on hardness. Hardness values are shown only for solution heat treated and precipitation hardened specimens, because these are more representative. Hardness of as cast specimens can be affected by cooling conditions, while solution heat treated specimens and annealed specimens can show similar hardness. (It should be considered that solution heat treated specimens are used for precipitation hardening. So a possible hardness difference can become more apparent). When we consider the effect of composition on hardness, we see that an increased silver concentration causes a decrease of hardness both in solution heat treated and hardened specimens.

In Figure 10 square dots represent hardness values of solution heat treated specimens. Triangles represent the maximum hardness attained after age hardening. Only the maximum hardness value is shown for each alloy, irrespective of the temperature and time required to attain it.

In our opinion, copper is the element showing the strongest effect on hardness. Zinc appears to have little effect on attainable hardness, or, better, it could affect hardness in a less direct way, by shifting the temperature and/or the time required to attain the maximum hardness, for a given copper concentration. This effect could be observed by examining the temperatures and times used for the hardening treatments, but we believe that this does not belong to the goals of this work.

Figure 11 shows the graph of hardness against the copper concentration for all the alloys, no one excluded.



Figure 11 – Graph of hardness against the copper concentration (wt‰)

It is evident that an increased copper concentration increases the hardness of solution heat treated specimens and also of the as cast material. In particular, the alloys can become age hardenable. A relatively low copper concentration (about 80 to 90%) can be sufficient to increase the hardness through an age hardening heat treatment.



Figure 12 – Graph of average grain size against the silver concentration (wt‰)

Grain size measurement, Figure 12, evidenced that alloys containing GR2 grain refiner show a fine grain structure approximately independent from the concentration of the main components. Things are more complicated for alloys containing GR1 grain refiner or deoxidizers, because there is not refining of the grain by GR1. This behavior could be expected, because GR1 grain refiner is cobalt, that is known to act in the solid phase. It means that cobalt seems to refine the grain or keep a refined structure after annealing, while in this work grain size has been evaluated in as cast alloys. Therefore we can say that refiner GR1 did not work correctly in investment cast specimens and the trend to grain refinement with increasing silver concentration could be ascribed to a corresponding decrease of cobalt solubility in the alloy.

In alloys containing deoxidizers a rule for the ef-

fect of silver concentration was not found. It is believed that, when deoxidizers are present, also zinc has an effect, favoring an increase of grain size. We can say that grain refiner GR2 is more important than the concentration of the main alloying elements, while deoxidizers tend to increase grain size and their effect is affected by the concentration of the main alloying elements.

In the following paragraphs we will consider the results for investment cast and wrought alloys separately.

18 ct colored gold alloys for investment casting

The 18ct alloys suitable for investment casting are twenty-one, namely alloys 3, 5, 8, 9, 10, 12, 14, 15, 17, 19, 20, 22, 24, 25, 26, 27, 28, 29, 31, 32 and 34.

Our experience says that alloys containing the GR1 grain refiner, more than 17,5% zinc and free from deoxidizers are not suitable for investment casting.

Tensile test have been carried out on investment cast alloys; the results for UTS and YS0.1 are shown in Figure 13.



Figure 13 – Graph of UTS and yield strength against silver concentration (wt‰)

A best fit curve (continuous curve) for UTS (triangles) and yield strength (square points) can be drawn for grain refined alloys (only GR2 grain refiner was used). The fit of the points is satisfactory and the strength decreases with increasing silver concentration.

An effect of silver concentration was not detected in the alloys containing deoxidizer additions, even if this could be ascribed to the narrow composition range. More generally, it could only be said that deoxidizer addition lowers both UTS and yield strength considerably, when compared with grain refined alloys. The UTS is notably more affected than the yield strength. The results (stars) appear to show that UTS increases with an increasing silver concentration: an explanation could be found in the hardness values we discussed before, Figures 10 and 11. Hardness tends to increase for lower silver concentrations (higher copper concentration): therefore the deoxidizer containing alloys (requiring a longer cooling time than grain refined alloys) become more brittle. This goes along with the everyday practice, where in 18 ct copper rich alloys (red gold) it is quite difficult to use deoxidizers, because of brittleness problems (these alloys cannot be rapidly cooled after casting).

Figure 14 shows the graph of elongation to rupture (E%) against silver concentration. Elongation is notably higher for grain refined alloys, and there is a small increase with increasing silver concentration, in agreement with the above described considerations. Elongation is much lower for deoxidized alloys and there is an increase with an increasing silver concentration. Zinc reduces elongation considerably for the same silver concentration. This result requires a deeper study, because the opposite effect could be expected. Maybe, in the deoxidized alloys, zinc could contribute to an increase of grain size with consequent lowering of elongation, but a wider concentration range should be studied to make this effect clear.



Figure 14 – Graph of elongation to rupture (E%) against silver concentration (wt‰)

18 ct wrought colored gold alloys

Twenty-four 18 ct colored gold alloys suitable for plastic deformation were studied, namely: 1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 13, 14, 15, 16, 18, 19, 21, 23, 26, 27, 30, 31, 32 and 34. Mechanical characteristics, drawability and work hardening curve were measured on these alloys.

The results for the tensile strength against silver concentration are shown in Figure 15.



Figure 15 – Graph of UTS and yield strength against silver concentration (wt‰)

There are two best fit curves for UTS (triangles): the upper curve refers to specimens grain refined with refiner GR2, while the lover curve refers to specimens containing the refiner GR1. The same holds true for the yield strength (lower curves square dots).

The refiner GR2 seems to be more efficient even if the difference between the two refiners seems to decrease with increasing silver concentration. With higher silver concentration the yield strength no more depends on the refiner type: it appears to confirm the trend observed for grain size.

A graph of the data on elongation to rupture is not shown, because they are all very similar and a correlation with alloy composition is not apparent. Elongation values were in the range of 27 to 32% for red gold and 31 to 34% with higher silver and zinc concentration.

Figure 16 shows the results of the deep drawing tests. It is not possible to find a clear effect of composition on drawability. In our opinion, this happened because drawability is affected by many parameters. We identified two main parameters, zinc concentration and grain size: the higher the zinc concentration the higher drawability will be. In figure 16 the alloys with higher zinc concentration (alloys 11, 16, 21 and 26) gave the highest drawability values. Alloy 14 gave an unexpected result, but this datum will be neglected for the moment.

It appears that, for the same zinc concentration, alloys with larger grain size are showing better drawability than alloys with finer grain size (with the same zinc concentration, alloys refined with GR1 show better drawability than alloys refined with GR2). Moreover it appears than drawability is increased by a higher silver concentration, i.e. softer alloys show higher drawability.

To get a deeper understanding of drawability a

wider experimentation should be carried out with carefully selected silver and zinc concentrations. Subsequently the same main alloying elements concentrations could be tested with the addition of the GR2 grain refiner.



Figure 16 – Graph of drawability against the silver concentration (wt‰)



Figure 17 – Work hardening best fit curves for 18 ct colored gold alloys

The work hardening curves, Figure 17, generally confirm the behavior of hardness of solution heat treated alloys, i.e. an increasing silver concentration (or a decreasing copper concentration) makes the alloys softer. Only the work hardening curves of alloys 3, 4, 18, 19, 27, 32 and 34 are shown in Figure 17, because they represent different concentrations of silver/copper. The other curves have been omitted to avoid confusion in the graph.

18 ct white gold alloys

Twenty-two white gold alloys were studied. Their compositions are listed in Table 4 as a function of nickel concentration (and, secondly, of zinc concentration). In Table 4 GR1 and GR2 are the same grain refiners already used for the 18 ct colored gold alloys.

Table 4 – Composition of the 18 ct investigated white gold alloys (weight %)

		1			1			
Spec- imen	Au	Ni	Zn	Cu	GR1	GR2	Deoxi- dizers	Ag
Alloy 1	750	25	25	Bal- ance				
Alloy 2	750	37,5	37,5	Bal- ance	Х			
Alloy 3	750	37,5	37,5	Bal- ance		X	Х	
Alloy 4	750	37,5	62,5	Bal- ance			Х	
Alloy 5	750	50	30	Bal- ance	Х			
Alloy 6	750	50	30	Bal- ance		X	Х	
Alloy 7	750	50	35	Bal- ance		Х	Х	5
Alloy 8	750	50	45	Bal- ance			Х	
Alloy 9	750	62,5	17,5	Bal- ance		Х		
Alloy 10	750	62,5	30	Bal- ance				
Alloy 11	750	62,5	30	Bal- ance		Х	Х	
Alloy 12	750	62,5	35	Bal- ance				
Alloy 13	750	62,5	35	Bal- ance			Х	
Alloy 14	750	75	35	Bal- ance				
Alloy 15	750	75	35	Bal- ance			Х	
Alloy 16	750	75	35	Bal- ance		X	Х	
Alloy 17	750	75	50	Bal- ance		X	Х	25
Alloy 18	750	87,5	37,5	Bal- ance				
Alloy 19	750	87,5	40	Bal- ance			X	
Alloy 20	750	100	25	Bal- ance		Х	Х	
Alloy 21	750	120	45	Bal- ance				
Alloy 22	750	120	45	Bal- ance			Х	

In this case too solidus and liquidus temperatures were measured for all the alloys, Figure 18. A general trend depending on nickel concentration was not found. Therefore in Figure 18 the alloys have been subdivided into 3 main groups, i.e. alloys with refiner GR1, alloys with refiner GR2 and alloys with deoxidizers (see Table 4). This behavior should probably be ascribed to the wide nickel and zinc concentration ranges: we can only say that liquidus and solidus temperatures seem to become higher with an increased nickel concentration. Zinc appears to lower these temperatures and the addition of deoxidizers mainly lowers solidus temperature.



Figure 18 – Graph of solidus and liquidus temperatures against nickel concentration (wt‰)

To obtain a better understanding of the correlation between composition and melting range, we considered alloys with GR2 and deoxidizer additions (suitable for investment casting) and alloys with GR1 and GR2 additions (suitable for cold working) separately. In the case of alloys for investment casting, Figure 19, solidus and liquidus temperatures seem to become higher with increasing nickel concentration for the alloys containing GR2. For the deoxidizer containing alloys liquidus and solidus temperatures seem first to increase and then decrease with increasing nickel concentration. Also the melting range appears to widen, going from alloys with GR2 additions to deoxidizer containing alloys. Moreover it is evident that solidus and liquidus temperatures of deoxidized alloys are lower than the corresponding temperatures in alloys with GR2 additions. We believe that this behavior could be ascribed to the fact that in the alloys containing only deoxidizer additions there is usually a higher zinc concentration that notably affects the melting range. Alloys 7 and 17 were not considered, because of the silver concentration (nickel concentration 50% and 75% respectively) that strongly lowers the melting temperature.



Figure 19 - Graph of solidus and liquidus temperatures against nickel concentration (wt‰) – Alloys for investment casting



Figure 20 – Graph of solidus and liquidus temperatures against nickel concentration (wt‰) – Wrought alloys

When considering wrought alloys, Figure 20, it can be seen that, in the case of GR1 containing alloys, the melting temperature first increases and then decreases with increasing nickel concentration. But the composition of alloy 21 is nearly similar to alloy 22 (for investment casting) and the anomalous behavior could be ascribed to the high zinc concentration. Effectively a higher zinc concentration – nickel concentration being the same – lowers the melting temperature of all alloys. Therefore it can be said that zinc notably affects the melting temperature.

Density is slightly lowered by an increased nickel concentration, Figure 21, but it could be considered as approximately constant, because the variation is very small, similar to the margin of error of the density measurement method. Also the effect of zinc on density is negligible.



Figure 21 – Graph of density against nickel concentration (wt‰)

The results for the color coordinates L^* , a^* and b^* are shown in Figures 22 to 26.



Figure 22 – Graph of L* against nickel concentration (wt%c)

Nickel appears not to have a clear effect on L^* , Figure 22, so a best fit curve was not drawn. Zinc concentration appears to be more important, and L^* appeared to increase with increasing zinc concentration, for the same nickel concentration, Figure 23.



Figure 23 – Graph of L* against zinc concentration (wt%)

Probably L^* is also affected by other additions – e.g. deoxidizers - , but experimental data are too scarce to reach a reliable conclusion.



Figure 24 Graph of a* against nickel concentration (wt‰)

Figure 24 shows the effect of nickel concentration on a*, but probably Ni + Zn concentration should be considered.



Figure 25 – Graph of a* against copper concentration (wt‰)

If the effect of copper on a* is considered a better fit is obtained, Figure 25, where the most discordant point corresponds to alloy 17, containing 25% silver.

A clear effect of nickel concentration on b^* can be seen, Figure 26, but in this case too there could be an additional effect of minor alloying additions, as in the case of L^{*}. If the graph of L^{*}, Figures 22 and 23, is compared with Figure 26, it appears that the relevant additions could be the same and also in the case of b^{*} an effect of deoxidizers is hypothesized.



Figure 26 – Graph of b* against nickel concentration (wt%)

Figure 27 shows the graph of hardness against nickel concentration. As for the colored gold alloys, hardness values of solution heat treated and precipitation hardened specimens are given. Hardness of solution heat treated specimens tends to increase with an increasing nickel concentration, while the maximum hardness of precipitation hardened material decreases. In this case too there is a remarkable scattering of the results and it is not easy to see a general trend. We believe that hardness could be strongly affected by the concentration of main alloying elements (ratio between nickel – zinc – copper) and negligibly affected by minor additions (such as refiners and deoxidizers), at least in our case.

Data scattering could be ascribed to the marked differences in zinc concentration. To find a useful correlation for production processes, we investigated the effect of copper concentration on hardness (this could correspond to considering the concentration of nickel added to zinc). The results are shown in Figure 28. It can be seen that, also in the case of white gold, copper enables to increase hardness after a suitable heat treatment. The hardness values of alloys 7 and 17 have been omitted in figures 27 and 28 because the addition of silver makes these alloys not comparable with the other alloys.



Figure 27 – Graph of hardness against nickel concentration (wt%)



Figure 28 – Graph of hardness against copper concentration (wt%)

Even if copper concentration is considered, drawing a good best fit curve is not easy. We believe that also in this case it could be ascribed to differences in zinc concentration. Therefore the curves are only approximated, because several data points were discarded, but an interpretation could be given. In our opinion the hardness of solution heat treated alloys decreases with an increased copper concentration. This effect can be verified in the everyday practice, where the feeling is that an increase of nickel concentration makes the alloy harder. As for the maximum hardness after precipitation hardening, the graphs seem to show that the alloys become precipitation hardenable with a minimum copper concentration of about 160%.

Regarding grain size, it is evident that GR2 is much more effective than GR1. It guarantees a consistently fine grain (about 100 μ m) irrespective of alloy composition. The trend of grain size with GR1 seems to confirm our results with 18 ct colored alloys: GR1 is not effective in investment casting and probably its effect improves with lower copper concentrations.

The behavior of grain size is more difficult to understand for deoxidized alloys. The best fit curve shows that average grain size decreases with increasing nickel concentration, down to the fine size obtained with GR2. This result was unexpected, because usually deoxidizers tend to increase grain size. It should be verified whether the grain refining effect depends on the nickel concentration only (see also alloys with GR1) or if nickel could form compounds with the deoxidizers that can act as grain refiners.



Figure 29 – Graph of average grain size against nickel concentration (wt‰)

The graph of nickel release rate against nickel concentration is shown in Figure 30. It can be seen that the addition of deoxidizers notably increases the nickel release rate, with the same main composition. The addition of the grain refiner has a beneficial effect on nickel release rate. Also silver addition to the alloy, with the same nickel concentration, reduces the nickel release rate. Therefore we confirmed the results of other works, i.e. that nickel release rate does not depend on nickel concentration only.



Figure 30 – Graph of nickel release rate against nickel concentration (wt‰)

18 ct white gold alloys for investment casting

Thirteen 18 ct white gold alloys for investment casting were studied, namely alloys 3, 4, 6, 7, 8, 11, 13, 15, 16, 17, 19, 20 and 22. We considered all alloys containing also deoxidizer additions as suitable for investment casting.

The results of the tensile tests are shown in Figure 31.



Figure 31 – Graph of UTS and yield strength against nickel concentration (wt‰)

The results from alloys 7 and 17 were not considered for drawing the best fit curves. Generally UTS and yield strength are higher for grain refined alloys than for alloys containing only deoxidizers. UTS and yield strength increase with increasing nickel concentration: UTS increase seems higher for deoxidized alloys. This result requires a confirmation, but it could be ascribed to a grain refinement effect related to the increase of nickel concentration. Generally a fine grain structure leads to improved strength characteristics.



Figure 32 – Graph of percent elongation to rupture against nickel concentration (wt‰)

Apparently an increase of nickel concentration causes a decrease of elongation to rupture. This could be related to the increase of UTS and yield strength of the alloys with GR2. In the deoxidized alloys elongation is more constant, even if alloy 22 shows a somewhat higher elongation. We believe that this behavior could be mainly related to zinc concentration, because deoxidized alloys usually contain more zinc than other alloys. Probably elongation should be related to nickel and zinc concentration and to grain size.

Wrought 18 ct white gold alloys

Fifteen of the studied 18 ct white gold alloys are suitable for plastic deformation, namely alloys 1, 2, 3, 5, 6, 7, 9, 10, 11, 12, 14, 16, 18, 20 and 21. All alloys not containing deoxidizer additions were considered as suitable for plastic deformation.

The results of tensile tests are plotted in Figure 33 against the nickel concentration. In this case too grain refined alloys show higher tensile strength. The GR2 grain refiner is clearly more efficient. UTS and yield strength increase with increasing nickel concentration.

A graph of the values of percent elongation to rupture is not shown, because all the values are quite similar and there is no appreciable effect of alloy composition. Elongation values are in the range 24 to 28%.



Figure 33 – Graph of UTS and yield strength against nickel concentration (wt‰)



Figure 34 – Graph of drawability against nickel concentration (wt‰)

The results of the deep drawing tests are plotted in Figure 34 against nickel concentration. Drawability decreases with increasing nickel concentration and is consistently lower for alloys containing GR2, as compared with alloys containing GR1. For the same nickel concentration, drawability increases with an increased zinc concentration.

Nickel and zinc concentration and grain size are the parameters affecting drawability more strongly.



Figure 35 – Work hardening curves for 18 ct white gold alloys

It has been found that an increase of nickel concentration goes along with an increased susceptibility to work hardening. Only the work hardening curves of alloys 1, 3, 11, 20 and 21 are shown in Figure 35, to have a clearer representation.

Conclusions

The above described results are only the first part of a much wider project.

After developing a suitable set of characterization tests, data for all concerned gold alloy caratages should be collected and analyzed. In this paper we described the characterization methods, and the data for 18 ct gold alloys are discussed. The data for 14 ct gold alloys are already available and the data for 9 and 10 ct alloys will be available before the end of 2010. Therefore information for all caratages will be presented in the following years. After concluding this part, we intend to determine the parameters having a more important effect in each production process, to be able to classify each composition with regard to the intended use. In this way, it will always be possible to recommend the most suitable composition for each use and, if the choice should be made on the basis of color, we should already know possible contraindications or processing limits.

Certainly the knowledge of physical and chemical characteristics of the alloys allows a comparison among the various compositions and enables to make a selection based on objective information and not on feelings or working habits.

As for the part presented in this paper, we believe that the characterization method we developed is suitable for our purposes. The required amount of material, the number of tests and the physical state of the alloys appear to guarantee a very good compromise between the data to be collected and the required time.

We believe that the data we collected are quite interesting and for several characteristics we succeeded to obtain a representation of the effect of the concentration of the main components of the alloys. The quality of the results seems to be good and only a few results departed from the expected trend. These are only a few and it could depend on experimental conditions. Certainly we should characterize tailor-made alloys to verify the observed trends more accurately: in particular this is true for white gold alloys.

These characterizations could also enable us to find the interconnection among different parameters, when a characteristic is affected by many parameters. For example zinc concentration could affect drawability in conjunction with grain size. It is obvious that also the effect of minor additions, such as grain refiners and deoxidizers, should be investigated for the sake of completeness. This work is not included in this project, but it should be carried out in the future.

Another point for investigation is to develop technological tests, but these also are less important in our priority list, that points to a basic characterization of precious gold alloys.

References

1. ASM Handbook, Vol. 2, "Properties and Selection: Non ferrous Alloys and Special-Purpose Materials"

2. Dieter Ott, In uence of Small Additions and Impurities on Gold and Jewerly Gold Alloys, The Santa Fe Symposium on Jewerly Manufacturing Technology 1997, 173-196

3. A. S. McDonald and G. H. Sistare, The Metallurgy of some Carat Gold Jewellery Alloys, Gold Bulletin, 1978, 11 (3), 66-73

4. W. S. Rapson, The Metallurgy of the Coloured Carat Gold Alloys, Gold Bulletin, 1990, 23 (4), 125-133

5. W. S. Rapson and T. Groenewald, "Gold Usage", Academic Press 1978

6. Benner L.S., Suzuki T., Meguro K., Tanaka S., "Precious Metals and Technology", International Precious Metals Institute

7. Reed-Hill R.E., Abbaschian R, "Physical Metallurgy Principles", Ed. Brooks/Cole

8. W. Nicodemi, "Metallurgia", Masson 1997